Spatial and temporal deposition of selected biogeochemical important trace species in South Africa

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Elne

Abstract

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The concern of potential adverse environmental effects due to increased anthropogenic emissions to the atmosphere necessitates the need for long-term atmospheric deposition programmes. Wet and dry depositions of emitted chemical species to the earth's surface play an essential role in controlling the concentration of gases and aerosols in the troposphere. The chemical content of atmospheric deposition is the signature of several interacting physical and chemical mechanisms such as emission and source amplitude; transport in and dynamics of the atmosphere; atmospheric chemical reactions; and removal processes. The importance of atmospheric deposition as a source of nutrients and key trace elements, i.e. nitrogen (N), sulphur (S), carbon (C) and base metals, is widely recognised (Duce *et al.*, 2009), while it could also be a source of toxic species (Greaver *et al.*, 2012). It is therefore important to establish atmospheric budgets of key chemical compounds to understand the functioning of ecosystems and biogeochemical cycles (Dentener *et al.*, 2006; Davidson *et al*., 2012). The study of deposition therefore allows for the tracing of the temporal and spatial evolution of atmospheric chemistry and is a pertinent indicator to evaluate natural and anthropogenic influences.

Atmospheric chemistry determines the natural and anthropogenic makeup and abundance of pollutant species such as aerosols and gases on a regional scale (Isaksen *et al.*, 2009). It is important to monitor the rates of deposition in order to assess the impact of deposited pollutants on terrestrial and aquatic ecosystems. This study focused on the total dry gaseous deposition and wet deposition of selected biogeochemically important trace species in South Africa. This study also contributed greatly to the database available for scientists in this field, since limited data on this subject is available for South Africa. This study includes measurement data for gaseous species as well as rainwater species in an attempt to assist future global deposition estimations.

The sites for the current study are Amersfoort (AF), Louis Trichardt (LT) and Vaal Triangle (VT) (located on the South African Highveld), and Skukuza (SK), which is situated in the South African Lowveld. These sites are considered to be regionally representative of the north-eastern interior of South Africa. Two of these sites are in the region where the major anthropogenic emission sources in South Africa are situated.

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Measurements of selected trace gases by using passive samplers were conducted at LT (1995-2014), AF (1997-2014), SK (2000-2014) and VT (2008-2014). Passive samplers were successfully deployed at SA DEBITS sites to measure monthly averages of atmospheric concentrations of sulphur dioxide (SO_2), nitrogen dioxide (NO_2), ammonia (NH_3), ozone (O_3) and nitric acid (HNO_3), with 90% of all samplers deployed resulting in usable results. The data illustrates the value and necessity of long-term air quality measurements at background sites.

The influence of a country's environmental policies and global awareness and focus on air pollution/prevention could be seen from a reduction in emissions of S and N pollutant gases up to 2003/2004, as well as the influence of socio-economic growth and international trade (international accreditation). The rapid industrial, economic and consumption growth in SA from 2002 to 2004 resulted in an increase in the emissions of gases. This was followed by the global financial crisis in 2007/2008 that influenced the production of large companies in SA, resulting in observed declines in the concentrations of gaseous species. Since 2010, a more pronounced increase was observed in the annual average concentrations at all sites. The increases can be attributed to high economic growth rates, which did not compensate for certain improvements, such as the incorporation of more stringent legislative application and the electrification of informal settlements.

Throughout the result section, it was evident that anthropogenic activities dominated at two sites, namely VT and AF, influencing the concentrations measured at these sites and indicating the impact of the industrial sector (e.g. coal-fired power generation, petrochemical industry and transport) on the country. The other two sites, SK and LT, showed more regional influences and indicated the effect of meteorological conditions on measurements (e.g. the anti-cyclonic circulation of pollutants from the two industrial sites).

Annual total gaseous dry sulphur deposition (contributed by SO_2) was 4.6, 7.1, 1.0 and 0.9 kgS/ha/a at AF, VT, SK and LT, respectively, correlating well with recent global assessments, with ranges between 4 and 12 kgS/ha/a (Vet, et al., 2014). Annual total gaseous dry nitrogen depositions (contributed by NO_2, NH_3 and HNO_3) were 16.7, 10.2, 4.2 and 4.0 kgN/ha/a at VT, AF, SK and LT, respectively. Deposition estimates were higher than modelled observations in the recent global assessment (Vet et al., 2014) at VT (especially for NO_2, which was estimated at 2-4 kgN/ha/a for Southern Africa) and both VT and AF were much higher compared to other African sites (Delon et al., 2010; Adon et al., 2013). This might be due to the strong industrial anthropogenic influence experiences at South African sites. Furthermore, it

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must be emphasised that bidirectional exchange was not taken into account and only the downwards deposition was considered.

Rain samples were collected at all four the sites from 2009 to 2014. The annual volume weighted mean indicated that the concentration of anthropogenically associated species was much higher at the two sites that are in close proximity to anthropogenic activities, while the concentrations of maritime and terrigenous species were higher at the two sites not directly impacted by major anthropogenic sources. Back trajectory analysis, however, did indicate that these two remote sites are also impacted by air masses passing over the source region through anti-cyclonic recirculation. In general, increases in the wet deposition of S and N were observed at all the sites compared to previous results reported. In addition, an increase in the H^+ concentration is observed at all the sites that are reflected in pH distributions, indicating more rain events with lower pH values. This could be ascribed to a significant increase in anthropogenic activities and population growth in this part of South Africa with an associated increase in energy demand.

An overall increase of wet deposition fluxes of species associated with anthropogenic activities in South Africa, i.e. sulphate (SO_4^{2-}), nitrate (NO_3^-) and ammonium (NH_4^+), was observed at the sites when the 2009 to 2014 results were compared to previous data reported by Mphepya *et al.* (2004; 2006). This increase can most likely be ascribed to the increase in anthropogenic activities in South Africa. Concurrently, the annual H^+ concentration increased since the previous publications., which is reflected in a shift to more acidic rain events at all the South African IDAF sites. Acidic potential calculations indicated that only 22 to 42% of the measured H^+ concentrations were neutralised by alkaline species at the various sites.

Abstract

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Keywords

Anthropogenic emissions, long-term atmospheric deposition, wet and dry deposition, ecosystems, biogeochemical cycles, passive sampling, precipitation, air pollution, air quality

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List of abbreviations and acronyms

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AF	Amersfoort
Amsl	Above mean sea level
APINA	Air Pollution Information Network for Africa
ARC	Agricultural Research Counsel
ARL	Air Resources Laboratory
AR5	The fifth assessment report of the Intergovernmental Panel on Climate Change
BTEX	benzene, toluene, ethylbenzene, and xylene
CAD	Composition of Asian Deposition
CSIRO	The Commonwealth Scientific and Industrial Research Organisation in Australia
DEA	Department of Environmental Affairs
DEAT	Department of Environmental Affairs and Tourism
DEBITS	Deposition of Biogeochemical Important Trace Species
DQOs	Data Quality Objectives
EC	electrical conductivity (Chapter 4)
EC	Eastern Cape Province
EF	enrichment factors
ESRL	Earth System Research Laboratory
FAO	Food and Agricultural Organisation
FS	Free State Province
GAW	Global Atmosphere Watch
GDAS	Global Data Assimilation System
GP	Gauteng Province

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HDPE	high-density polyethylene
HPA	Highveld Priority Area
HYSPLIT	Hybrid Single-Particle Lagrangian Integrated Trajectory
IC	Ion Chromatography
ICDA	International Chromium Development Association
ID	Ion Difference
IDAF	International DEBITS Africa
IGAC	International Global Atmospheric Chemistry
IPCC	Intergovernmental Panel on Climate Change
ISO	International Organisation for Standardisation
ITCZ	Inter-tropical Convergence Zone
IVL	Swedish Institute for Environmental Research
KNP	Kruger National Park
KZN	Kwazulu Natal Province
LIS	bi-annual inter-laboratory comparison study
LP	Limpopo Province
LT	Louis Trichardt
MP	Mpumalanga Province
NBRO	National Building Research Organisation, Sri Lanka
NC	Northern Cape Province
NCEP	National Centre for Environmental Prediction
NF	Neutralisation Factor
NOAA	National Oceanic and Atmospheric Administration
NUS	National University of Singapore
NW	North-West Province

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NWU	North-West University
OA	Organic Acids
pA	Acidity Potential
PBL	planetary boundary layer
PCA	principal component analysis
PM	Particulate Matter
PTFE	Polytetrafluoroethylene
QA	Quality Assurance
QC	Quality Control
RAPIDC	Regional Air Pollution in Developing Countries
RF	Radiative forcing
SA	South Africa
SAFARI-92	Southern Africa Fire-Atmosphere Research Initiative (1992)
SHPZ	Subtropical High Pressure Zone
SK	Skukuza
UP-SL	University of Peradeniya, Sri-Lanka
US EPA	United States Environmental Protection Agency
V_d	Deposition Velocity
VOCs	Volatile organic compounds
VT	Vaal Triangle
VTAPA	Vaal Triangle Air-shed Priority Area
VWM	Volume Weighted Mean
WC	Western Cape Province
WD	Wet Deposition
WHO	Word Health Organisation

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WMO   The World Meteorological Organization

%PCL   Percentage precipitation covering length

%TP   Percentage total precipitation

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Chapter 1: Introduction

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In this chapter, a brief summary of the global perspective on the necessity of regional air quality monitoring programmes as well as areas of uncertainty and gaps is presented. This is followed by a summary on the local perspective, leading to the motivation/statement of need and a description of this study, including the aims and objectives. The chapter is concluded by a short overview of the format of the thesis with a description of each of the following chapters and what they entail.

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1   Global perspective on air pollution

1.1   Introduction

Air pollution is not a new term associated with the modern world and can be traced back several centuries. Documented examples of air pollution episodes, for example, date back as early as 1930, where thousands of people fell sick and 63 died in Belgium (the Meuse River Valley) due to fog that was trapped by thermal inversion over a 15-mile stretch of the valley (Fenger, 1999; Brimblecombe, 1987). As air pollution became a more severe, persistent problem in large cities later in the previous century, the focus of atmospheric chemistry research shifted towards the identification of sources, the properties of pollutant species in the atmosphere and the effects thereof (Wallace & Hobbs, 2006).

Air pollution has numerous definitions, such as: *"Any atmospheric condition in which substances are present at concentrations high enough above their normal ambient levels to produce a measurable effect on man, animals, vegetation or materials. "Substances" implies any natural or man-made chemical elements or compounds capable of being airborne. These substances may exist in the atmosphere as gases, liquid drops or solid particles."* (Seinfeld, 1986); Also *"when gases or aerosol particles emitted anthropogenically, build up in concentrations sufficiently high to cause direct or indirect damage to plants, animals, other life forms, ecosystems, structures or works of art"* (Jacobson, 2002).

Air pollutants can lead to diverse impacts on human health, ranging from nausea and skin irritations to athma, cancer, birth defects and impacts on the immune system (Kampa & Castanas, 2008). Most developed countries, as well as developing countries, have legislature to improve air quality and to limit the effects of air pollution on human health. "*Clean air is considered to be a basic requirement of human health and well-being. However, air pollution continues to pose a significant threat to health worldwide*" (WHO, 2005). Humans come into contact with air pollution via three exposure routes, namely inhalation, ingestion and dermal contact (Kampa & Castanas, 2008). Air pollutant effects on the respiratory system include irritation, bronchoconstriction, asthma, lung inflamation and even lung cancer (Kampa & Castanas, 2008). The effects on the cardiovascular system include reduced oxygen availability, blood coagulation, blood clotting, increased blood pressure, anaemia as well as heart disease (Kampa & Castanas, 2008).

Another term that has become synonymous with atmospheric pollution, is *smog,* which is derived from the words smoke and fog. This term was originally used in association with heavy air pollution events in cities, but recently has been applied to all forms of severe air pollution that limit visibility in large cities and urban areas (Wallace & Hobbs, 2006). One of the more popular examples of smog is the so-called London smog that occurred in 1952. Cold air produced a temperature inversion layer that trapped acid aerosols in a dense fog that lasted for five days and more than 4 000 people died from respiratory diseases (Brimblecombe, 1987; Fenger, 1999).

Although scientific and public awareness of air quality has increased, the above-mentioned example from literature emphasise the necessity to effectively control and monitor air pollution and acceptable air quality worldwide.

1.2   Types of air pollutants

A large number of air pollutant species are present in the atmosphere, with a variety of different chemical compositions, sources and chemical properties (e.g. reaction rates, transformations, atmospheric stabilities and transport properties) (Kampa & Castanas, 2008). Pollutant species are further classified as primary or secondary pollutants. Pollutants that are emitted directly into the atmosphere are called primary pollutants, while secondary pollutants are formed in the atmosphere from primary pollutants (precursors). Although air pollutants are different, they share certain properties

that enable us to group them together. In general, these pollutant species are divided into two groups, namely *gaseous* species and *aerosol* species (also refered to as *particulate matter*).

1.2.1 Gaseous

Gaseous pollutants consist of organic and inorganic compounds. Typical organic compounds include volatile organic compounds (VOCs), methane (CH_4), non-methane hydrocarbons, and halogenated gases, among others. The most important inorganic compounds are NO_2, N_2O, SO_2, O_3, CO, and CO_2 (Kampa & Castanas, 2008). A major source of gaseous pollutants is the combustion of fossil fuels, which emit NO_x, SO_2, CO, CO_2, and VOCs into the atmosphere. All of these species induce further chemical reactions in the troposphere, which could lead to the formation of harmful and more toxic compounds (Graedel & Crutzen; 1997).

1.2.2   Aerosol

Aerosols are the suspension of small solid or liquid particles in the atmosphere, with different sizes, morphology, number, shape and chemical composition (Kampa & Castanas, 2008). Particles less than 2.5µm in aerodynamic diameters are often referred to as fine particles, or $PM_{2.5}$. Particles with aerodynamic diameters larger than 2.5µm and less than 10µm are generally referred to as coarse particles, or PM_{10}.These particles have further been categorised according to their aerodynamic particle diameter, e.g. ultra-fine (<0.1µm), fine (0.1µm up to 1µm) and coarse (>1µm) particles (Kampa & Castanas, 2008). Aerosol particles originate from a variety of both natural (e.g. dust plumes, volcanic eruptions, sea spry) and/or anthropogenic sources (e.g. mining, combustion, power generation, transport, industry). Primary particles are emitted directly from a source as a solid or liquid particle, whereas secondary particles are formed by other processes that take place in the atmosphere (Pöschl, 2005).

1.3   Pollutant sources

Atmospheric pollutants can originate from natural (e.g. vegetation, soil and dust, oceans or aquatic surfaces and sea spray, volcanoes, decomposition of organic matter) or anthropogenic (e.g. fossil fuel combustion, traffic, household combustion, petrochemical activities, mining, agricultural activities) sources (Williams & Baltensperger, 2009).

Anthropogenic and natural emissions do not necessarily follow the same temporal trends, and their composition also differs with spatial variation. Anthropogenic emissions, for instance, are largely governed and influenced by a country's air quality legislation enforcement, as well as economic well-being (Isaksen *et al.*, 2009). While anthropogenic emissions have declined in European countries and the USA, the struggle for developing countries remains to find a balance between sustainable development and air quality. Natural emissions, on the other hand, show large inter-annual variations and are strongly influenced by changes in the climate (Isaksen *et al.*, 2009). The climate and atmospheric chemical composition of a region directly influence the stability of the ecosystem and are critical to consider in sustainable development (Laj *et al.*, 2009).

1.4 Pollutant deposition

The atmospheric deposition of emitted chemical species and secondary products to the earth's surface through wet and dry processes plays an important role in controlling the concentrations of pollutants present in the troposphere. Deposited species can provide essential nutrients to ecosystems or can cause disturbances. The chemical content of atmospheric deposition is the signature of several interacting physical and chemical mechanisms, such as: emission and source strength; transport in and dynamics of the atmosphere; atmospheric chemical reactions; and removal processes (Lacaux & Artaxo, 2003). The study of deposition therefore allows for the tracing of the temporal and spatial evolution of atmospheric chemistry and is a pertinent indicator to evaluate natural and anthropogenic influences. Changing anthropogenic influences are more easily observed in the developing world due to the rapid increase in population growth and associated energy demands. Acid deposition primarily results from the transformation of sulphur dioxide (SO_2) and nitrogen oxides (NO_x) into dry or wet secondary pollutants such as sulphuric acid (H_2SO_4) (Shallcross, 2009), ammonium nitrate (NH_4NO_3) and nitric acid (HNO_3) (Atkinson, 2000). These species can be transported hundreds of kilometres from their origin.

1.5 Atmospheric chemistry and air quality

In a fast developing and growing world, with numerous challenges regarding air quality, climate change and sustainable development, it is of extreme importance to understand numerous aspects regarding the atmospheric sciences (WMO/GAW, 2007; Laj *et al.*, 2009). The World Meteorological Organization (WMO) emphasises the importance of monitoring the chemical and physical composition and characteristics of the atmosphere, both on global and regional scale, to understand and contribute to scientific assessments, to make environmental policies and to predict the future state of the environment (WMO/GAW, 2007). These observations and analyses are needed to advance the scientific understanding of the effects of increasing influence of human activity on the global atmosphere and a subsequent impact of these changes on human health and ecosystems (WMO, 2017).

Atmospheric chemistry determines the natural and anthropogenic makeup and abundance of pollutant species such as aerosols and gases on a regional scale (Isaksen *et al.*, 2009). It is important to monitor the rates of deposition in order to assess the impact of deposited pollutants on terrestrial and aquatic ecosystems. Figure 1.1 provides an illustration of some of the atmospheric processes that occur and

affect air quality. Deposition rates of atmospheric pollutants provide valuable information on pollution loads in the atmosphere, and how atmospheric chemistry has been altered by human activities.
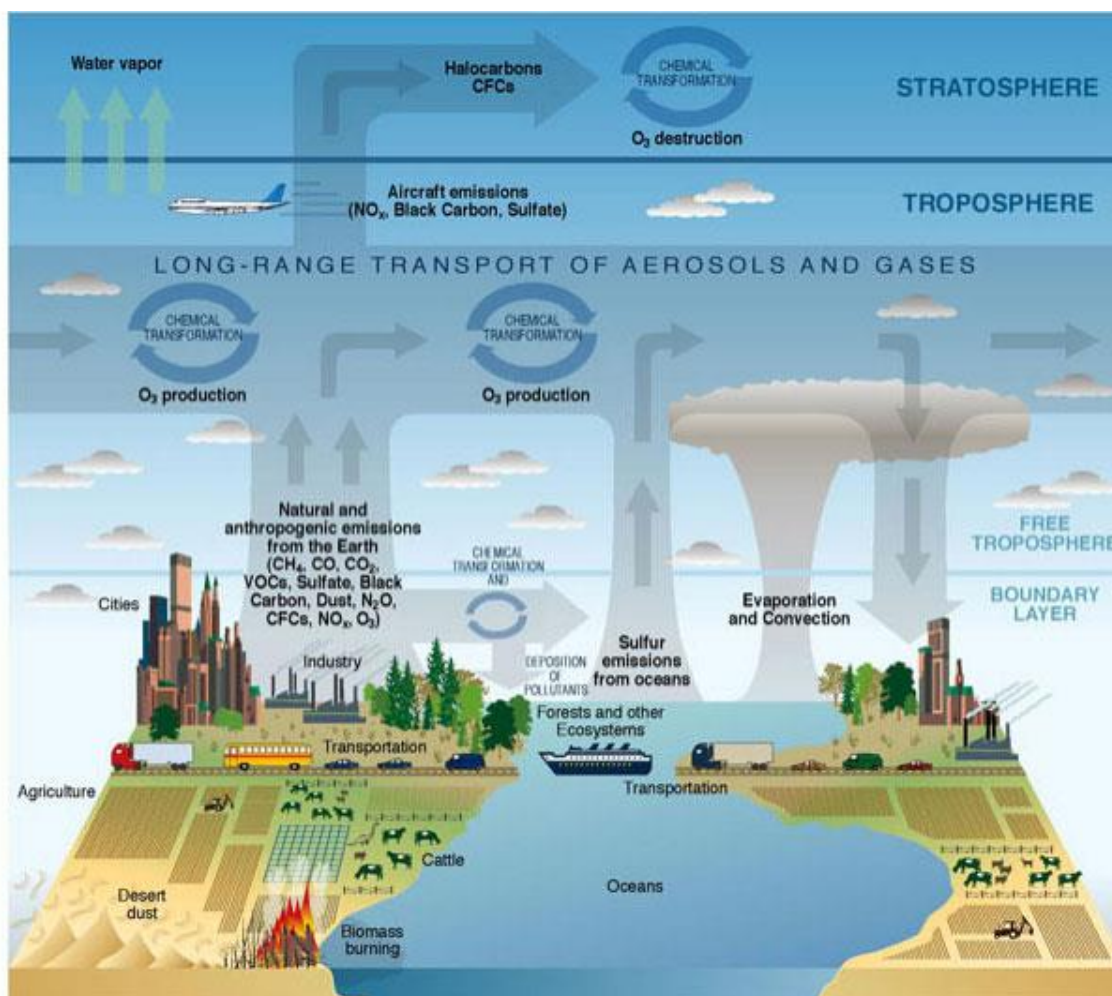
Figure 1.1: Illustration of some typical atmospheric processes that takes place and impact regional as well as global air quality

(https://www.learner.org/courses/envsci/visual/visual.php?shortname=atmospheric_processes) Courtesy United States Climate Change Science Program (Illustrated by P. Rekacewicz).

Although the focus of the study is **not** climate related, it is necessary to understand the link between the study parameters and climate at a global level. Numerous anthropogenic emissions result in a changing atmospheric composition, which necessitates scientists to research the changes that occur in an effort to understand the implications thereof (Laj *et al.*, 2009). According to the fifth assessment report (AR5) of the Intergovernmental Panel on Climate Change (IPCC), the earth's surface temperature has continued to increase successively over the last three decades, the ocean has been warming since 1971,

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Greenland and Antarctic ice is melting, the rate of sea level rise has increased, and atmospheric concentrations of carbon and other biogeochemical species have increased substantially (IPCC, 2013).

The change in atmospheric composition affects (among others) climate, atmospheric processes, human health, the hydrological cycle, ecosystems, economies and the adaptability of governments to changes on societal and environmental levels (Laj *et al.*, 2009). Drivers of climate change can be classified as the natural and/or anthropogenic substances and processes that change the energy budget of the earth. Radiative forcing (RF) is a means to quantify the change in energy caused by these drivers. Positive RF causes surface warming, while negative RF leads to surface cooling (IPCC, 2013). RF values stated in the IPCC AR5 (Figure 1.2) are estimated based on observations, properties of gases and aerosols, calculations and modelled observations.
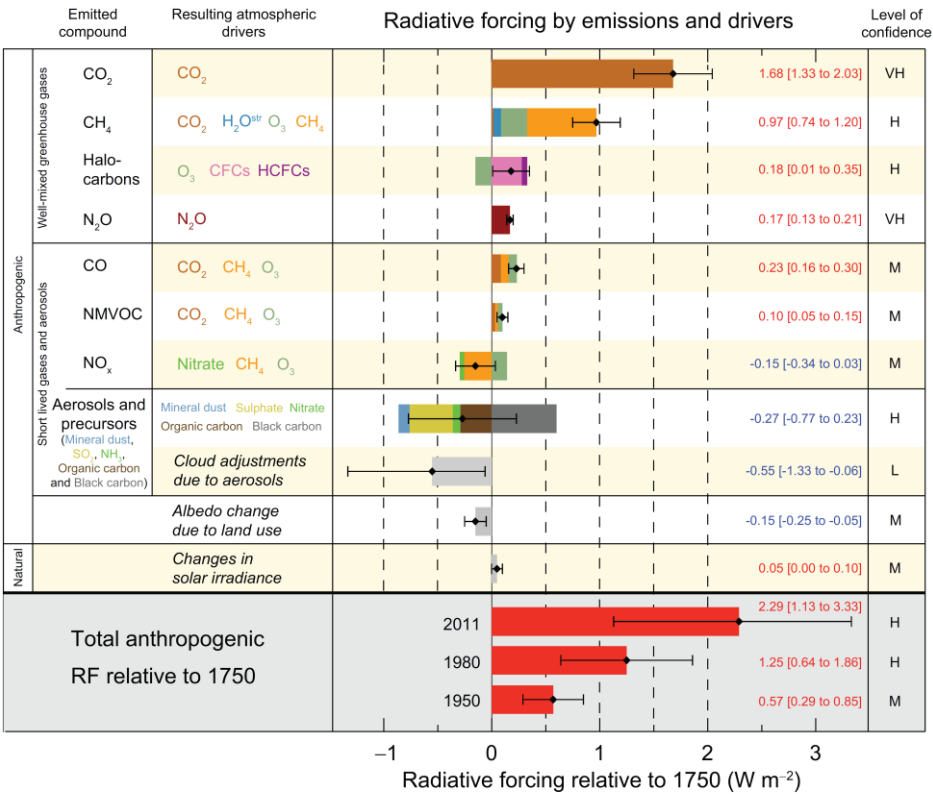
Figure 1.2: Radiative forcing estimates in 2011 relative to 1750, with aggregated uncertainties for the main drivers of climate change (IPCC, 2013).

Trace gases and aerosols have a significant RF effect that can either result in a net cooling or heating of the atmosphere. Aerosol particles cause these effects because they scatter and absorb radiation from

the sun and the earth. They are also involved in the formation of clouds and of wet precipitation (Pöschl, 2005). Aerosols can influence climate in a direct (interactions of radiation and temperature on particles) or indirect (cloud and precipitation modifications by aerosols) manner, with regards to RF. (Pöschl, 2005; Andreae, 2007).

Figure 1.2 (IPCC, 2013) shows the RF estimates in 2011 relative to 1750, calculated on global average RF, partitioned according to the emitted compounds or processes that result in a combination of drivers. The best estimates are indicated on the figure as black diamonds, coupled with the corresponding uncertainty levels and values in red (on the right-hand side). The levels of scientific confidence are indicated on the far right of the figure (VH = very high, H = high, M= medium, L = low, VL = very low). Total anthropogenic radiative forcing is provided for three dates (i.e. 1950, 1980 and 2011) relative to 1750 at the bottom of the figure (IPCC, 2013). According to these estimates, the total radiative forcing is positive, causing an increase in energy uptake by the climate system that can largely be attributed to an increase in atmospheric CO_2 concentrations since 1750 (IPCC, 2013).

2 Local perspective on air pollution

2.1 Introduction

The Deposition of Biogeochemically Important Trace Species (DEBITS) task of the International Global Atmospheric Chemistry (IGAC) programme was initiated in 1990 in collaboration with the Global Atmosphere Watch (GAW) network of the World Meteorological Organisation (WMO) to investigate long-term concentrations and deposition (wet and dry) of chemical species in the atmosphere in the tropics (Lacaux et al., 2003). The DEBITS programme is currently continuing within the new IGAC structure or DEBITS II (Pienaar et al., 2005). The African component of this initiative is known as IGAC DEBITS Africa (IDAF) and consists of ten strategically positioned deposition sites in southern and western Africa that are representative of important African ecosystems (http://idaf.sedoo.fr/spip.php?rubrique45).

South Africa is a country that shows both characteristics of a developed, as well as a developing country. Many challenges associated with economic and population growth influence local policies on air quality management, sustainable development and conservation of the ecosystem. The Mpumalanga Highveld and Gauteng account for more than 90% of SA's scheduled emissions of SO_2 (approx. 2 million tons per year), NO_2 (approx. 1 million t/year) and particulates (approx. 0.3 t/year) (Wells *et al.*, 1996). Energy

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production in South Africa accounts for approximately 70% of the country's SO_2 emission, 55% of NO_x and 36% of particulate matter (PM), while emissions from other industrial, commercial and fossil fuel consuming processes contribute approximately 27% SO_2, 23% NO_x and 44% PM. Other contributions to SO_2, NO_x and PM include biomass burning (0%, 0.3% and 6%, respectively) and domestic burning (0.8%, 0.2% and 9%, respectively) ((DEA), 2012; Scorgie *et al.*, 2004).

2.2   South African legislation and air pollution priority areas

The Air Quality Act 39 of 2004 has made provision for the identification of priority areas (illustrated in Figure 1.3), where the air quality is regarded as poor and detrimental to human health and the environment. Currently, there are three such areas identified within South Africa, of which two are of concern for this study. The Vaal Triangle Air-shed Priority Area (VTAPA) was declared as the first priority area in South Africa by the Minister of Environmental Affairs and Tourism on 21 April 2006. The VTAPA includes areas contained in four different local municipalities over two provincial boundaries. The area includes heavy industrial activities, one power station, several commercial operations, motor vehicle emissions, as well as many households that utilise coal as an energy source. (DEAT, 2009). The Minister of Environmental Affairs and Tourism proclaimed eastern Gauteng and western Mpumalanga as a national priority area termed the Highveld Priority Area (HPA) on 23 November 2007 (DEA, 2012). The Mpumalanga Highveld is known (Held *et al.*, 1996) for its diverse anthropogenic activities, which include agriculture, metallurgical and mining operations, petrochemical plants, power generation, coal dumps, and transportation (Freiman & Piketh, 2003). These activities contribute to elevated levels of organic and inorganic gaseous species, which include benzene, toluene, ethylbenzene, and xylene (BTEX), as well as NO_2, SO_2, and O_3.
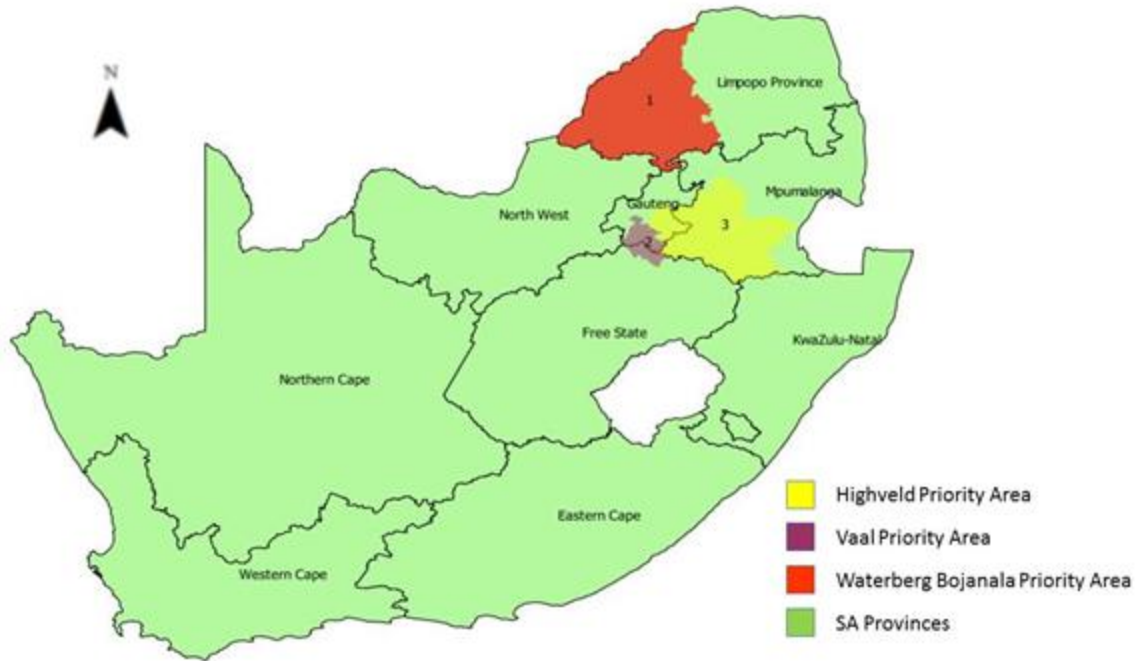
Figure 1.3: Priority areas in South Africa (http://www.saaqis.org.za/Images/PAs%20South%20Africa4.jpg)

3   Motivation/statement of need for the current study

Concern about potential adverse environmental effects due to increased anthropogenic emissions to the atmosphere necessitates the need for long-term atmospheric deposition programmes. Wet and dry depositions of emitted chemical species to the earth's surface play an essential role in controlling the concentration of gases and aerosols in the troposphere. The study of deposition therefore allows for the tracing of the temporal and spatial evolution of atmospheric chemistry and is a pertinent indicator to evaluate natural and anthropogenic influences.

A reasonable amount of research on atmospheric chemistry has been conducted in southern Africa. Many institutions, both local and international, have done, and/or are still doing research on air quality in the region. Although the amount of research done in the field is increasing, there are still many uncertainties, and a great deal of research that has been done elsewhere in the world has not been conducted in South Africa yet.

Previous studies in South Africa that are related to this particular study included measurements of ambient gaseous species and aerosols (dry deposition) (Turner *et al.,* 1995; Zunckel *et al.,* 1996; Zunckel, 1999; Mphepya, 2002; Mphepya & Held, 1999; Kleynhans, 2008; Adon *et al.*, 2010; Carmichael *et al.*, 2003; Dhammapala, 1996; Josipovic, 2009; Laakso *et al.*, 2012; Lourens *et al.*, 2011; Lourens *et al.*, 2012; Martins *et al.,* 2007; Martins, 2009) and precipitation chemistry (wet deposition) (Turner, 1993; Turner *et al.,* 1996; Held *et al.,* 1999; Mphepya, 2002; Mphepya *et al.,* 2004; Mphepya *et al.,* 2006). However, in a recent global assessment of precipitation and deposition, a large gap in measurement data was observed for the African continent. The authors of this assessment had to include data outside the scope of the article in order to have some data available for the continent (Vet *et al.*, 2014). This current study will aim to address this gap and to aid future global assessment reviews with measurement-based results from South Africa.

This study will focus on the dry gaseous and wet deposition of selected biogeochemically important trace species in South Africa. Therefore, it will contribute greatly to the database available for scientists in this field, since limited data on this subject is available for South Africa. This study includes measurement data for gaseous species as well as rainwater species in an attempt to assist future global deposition estimates. Furthermore, this study will contribute new data on precipitation chemistry, since wet deposition was previously only measured at a very limited number of sites in South Africa from

1999 until 2002. An added value of the current study is the long-term data that is available for selected gaseous species.

4   Aim, objectives and approach of current study

4.1   General aim

Considering the shortage of long-term data and specifically deposition data for South Africa, the general aims of this study are to measure the concentrations of selected gaseous species using passive samplers and to quantify the concentrations of chemical species in rainwater, as well as deposition estimates thereof. Furthermore, the study will aim to provide valuable measurement data for fellow researchers that will partially alleviate the shortage of available data for the African continent.

4.2   Research objectives

Considering the overview of available literature and gaps, as indicated in the previous sections, the key objectives of this study are to:

1. determine the long-term ambient concentrations of selected inorganic gaseous species, namely SO_2, NO_2, O_3, HNO_3 and NH_3, at four sites in the South African interior;

2. determine the chemical composition and concentrations of precipitation (specifically the following ionic species: acetic acid, propionic acid, formic acid, chloride, sulphate, nitrate, oxalic acid, sodium, potassium, magnesium, calcium and ammonium) at all sites considered;

3. estimate the dry gaseous and wet deposition of the measured sulphur and nitrogen species at the selected sites;

4. evaluate differences in concentrations (for both trace gases as well as precipitation) between the selected sites;

5. evaluate temporal differences in concentrations at the selected sites; and

6. calculate source group contributions of the above-mentioned species at the selected sites.

4.3 Approach of the study

The scientific activities are mainly based on measurements of precipitation in order to quantify wet deposition, as well as gaseous concentrations in order to estimate dry gaseous deposition. A detailed description of the selected sites (namely Vaal Triangle, Amersfoort, Louis Trichardt and Skukuza) and instrumentation will be presented in Chapter 2. The selected deposition sites are representative at regional scale and were equipped with instrumentation to measure meteorological parameters. Each site was created and maintained with the goal of producing long-term time-series data.

A set of existing and published experimental and analytical protocols was defined to assure data quality, and to ensure the inter-comparison of the measurements of wet and dry deposits within the international science community. Wet deposition measurements were accomplished according to a standardised rainwater sampling, preservation and chemical analysis procedure. To obtain comparable datasets for precipitation chemistry with a high quality assurance, an experimental strategy comprising the following steps was employed:

- wet-only sampling for rain days;
- preservation of the chemical content by freezing;
- quality assurance by using the US EPA criteria based on ionic and conductivity balances;
- annual analytical laboratory performance checks participating in the biannual WMO rainwater chemical analysis inter-comparison;

Dry deposition quantification for gases was accomplished through the monitoring of concentrations by passive gas sampling for SO_2, NO_2, NH_3, HNO_3 and O_3 and using standardised chemical analysis. The performance of the passive samples was also confirmed by participating in an international inter-comparison study that was initiated by the WMO.

5 Structure of the thesis

The thesis is structured in such a way that the relevant literature for both dry and wet deposition is covered in the beginning of the chapters dealing with these topics while the general discussions regarding the regional climate and experimental design is covered in a separate chapter.

5.1 Chapter 2: Regional climate and experimental design

This chapter starts off with a brief discussion on the regional climate and air mass transport of South Africa. This will include discussions on air circulation, the formation of stable layers, regional climate and rainfall. Thereafter, the selection of sites, as well as description and discussion on the geographical context, vegetation, local point sources of interest and the population density in the area of the sites is presented. The chapter is concluded with protocols for gaseous and precipitation measurements, respectively. Each of these protocols includes apparatus used, collection of samples, chemical analyses and quality control/quality assurance (QC/QA) procedures.

5.2 Chapter 3: Gaseous measurements and dry deposition estimations by using passive sampling

Chapter 3 starts off with a general introduction to trace gases, focusing on the historical perspective and the importance of trace gases, health and environmental impacts, biogeochemical cycles and the selected gaseous species for this study (namely SO_2, NO_2, NH_3, HNO_3 and O_3). The general properties, atmospheric lifetime and importance of these species will be briefly discussed, as well as natural and anthropogenic sources, and the lifecycle of the gaseous species. The results and discussions include contextualising results from this study to other SA, African and international studies, a discussion on the long-term measurement results and deposition estimates from a temporal and spatial perspective and finally a discussion on inter-annual variability (seasonal trends).

5.3 Chapter 4: Assessment of precipitation chemistry and wet deposition

Chapter 4 focuses on the wet deposition measurements of the current study. This chapter starts off with a brief discussion on relevant literature in die field of precipitation chemistry and acid rain. Comparisons between previous SA studies and the current study will be made, as well as comparisons between South

African sites and other African sites. Different statistical methods were employed to quantify the influence of different sources and processes.

5.4 Chapter 5: Total gaseous dry and wet deposition of nitrogen and sulphur compounds

This chapter focuses on combining measurements obtained from Chapter 3 (gaseous) and Chapter 4 (precipitation) in order to roughly estimate the total dry gaseous and wet deposition of nitrogen and sulphur species at the selected sites. Furthermore, this estimation is compared to values reported in a recent global assessment study (Vet *et al.*, 2014).

5.5 Chapter 6: Critical assessment and concluding remarks

This chapter focuses on the most important recommendations from each of the chapters and critically evaluates whether the objectives of the current study were met, as well as to what extent the motivation/statement of need for the study was addressed. Furthermore, remaining gaps will be identified and recommendations are made to aid future research in South Africa on related topics.

Chapter 2: Experimental

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In this chapter, an overview of the regional climate and air mass transport is presented, followed by a description of the sites and an overview of the sampling techniques, analytical techniques and the quality control/quality assurance measures that were taken.

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1 Regional climatology and meteorology of Southern Africa

The specific climatology of a region is very important since it has an important impact on pollutant concentrations (e.g. temperature and water vapour influence ozone concentrations). South Africa is situated in the subtropical high pressure belt and is influenced by several high-pressure cells, in addition to various circulation systems prevailing in the adjacent tropical and temperature latitudes. Furthermore, South Africa has a wide range of climatic and hydrological regions. The following sections will aim to provide a brief overview of the climatology and meteorology of South Africa (SA).

1.1 Meteorology

Figure 2.1 illustrates the differences between the summer and winter atmospheric pathways of synoptic systems that drive rainfall events over South Africa, as well as air mass circulation and transport. The predominant circulation of the atmosphere over the South African interior (Figure 2.1) is anti-cyclonic, due to the dominance of three high pressure cells (i.e. the South Atlantic high pressure cell off the west coast, the South Indian high pressure cell off the east coast, and the continental high pressure cell over the interior) (DEAT, 2009). Furthermore, the seasonal north-south migration of the Inter-tropical Convergence Zone (ITCZ), the Subtropical High Pressure Zone (SHPZ) and the Temperate Zone drives the seasonal rainfall distribution over southern Africa, which is therefore highly variable and manifests as prominent summer/winter cycles (Figure 2.1) (Van Wyk *et al.*, 2011).
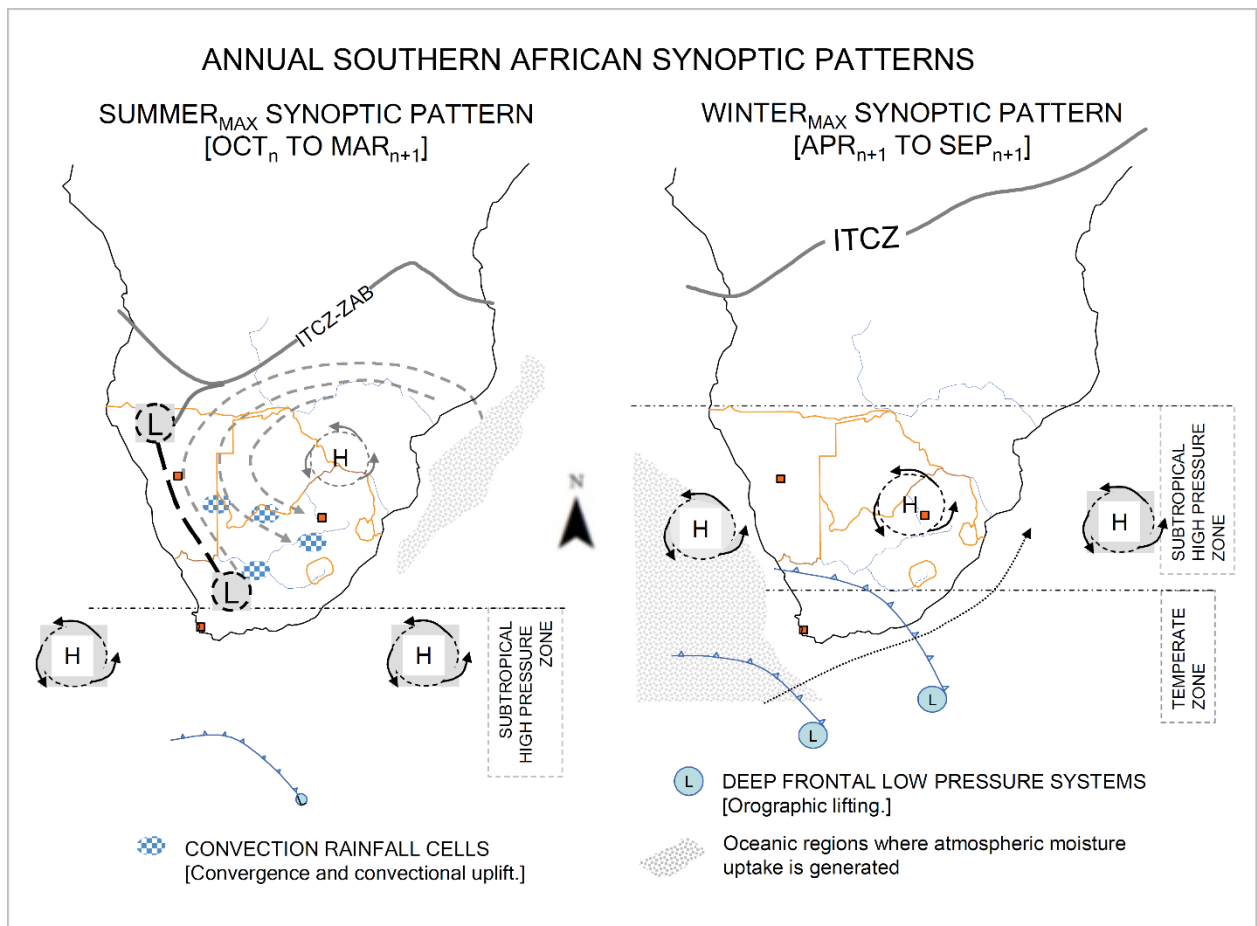
Figure 2.1: Synoptic patterns over SA during summer and winter, in relation to the generation of airborne moisture and the general migration pathways (Van Wyk, *et al.*, 2011)

During the summer months (December-February), the anti-cyclonic belt weakens and shifts southwards (Figure 2.1), allowing the tropical easterly flow to resume its influence over South Africa. The summer is characterised by low air pressure conditions that prevail over the interior, generally unstable meteorological conditions and an increase in vertical motion and dispersion of pollutants in the atmosphere (Tyson *et al.*, 1996). In the summer months, the first elevated inversion is known to increase to between 4 and 5 km over the plateau.

The winter weather of South Africa (June-August) is largely dominated by perturbations in the westerly circulation (Figure 2.1). Such perturbations take the form of a succession of cyclones or anti-cyclones moving eastwards around the coast or across the country (DEAT, 2009). The winter is characterised by more stable conditions and lower wind speeds over most of South Africa. Winters are also characterised by the formation of inversion layers that suppress the vertical dispersion of pollutants in the atmosphere by reducing the height to which such pollutants are able to mix and therefore concentrating these pollutants between these layers (Tyson *et al.*, 1996). During the

Chapter 2

winter months, the first elevated inversion is located at an altitude around 3 km over the plateau. However, several thermally-induced inversions occur, with the lowest being approximately 100m above ground level (Gierens *et al.*, 2017).

Previous studies regarding the atmospheric circulation over southern Africa have identified four major synoptic circulation types (Krishnamurti *et al.*, 1993; Garstang *et al.*, 1996; Piketh & Walton, 2004) that influence the atmospheric transport of pollutant species. These types include the semi-permanent subtropical continental anticyclones, transient mid-latitude ridging anticyclones, westerly baroclinic disturbances and baratropic quasi-stationary tropical easterly disturbances. Figure 2.2 illustrates the sub-continental atmospheric circulation as determined from a five-year trajectory analysis (1990-1994) (originating from the Mpumalanga Highveld) by Piketh and Prangley (1998).
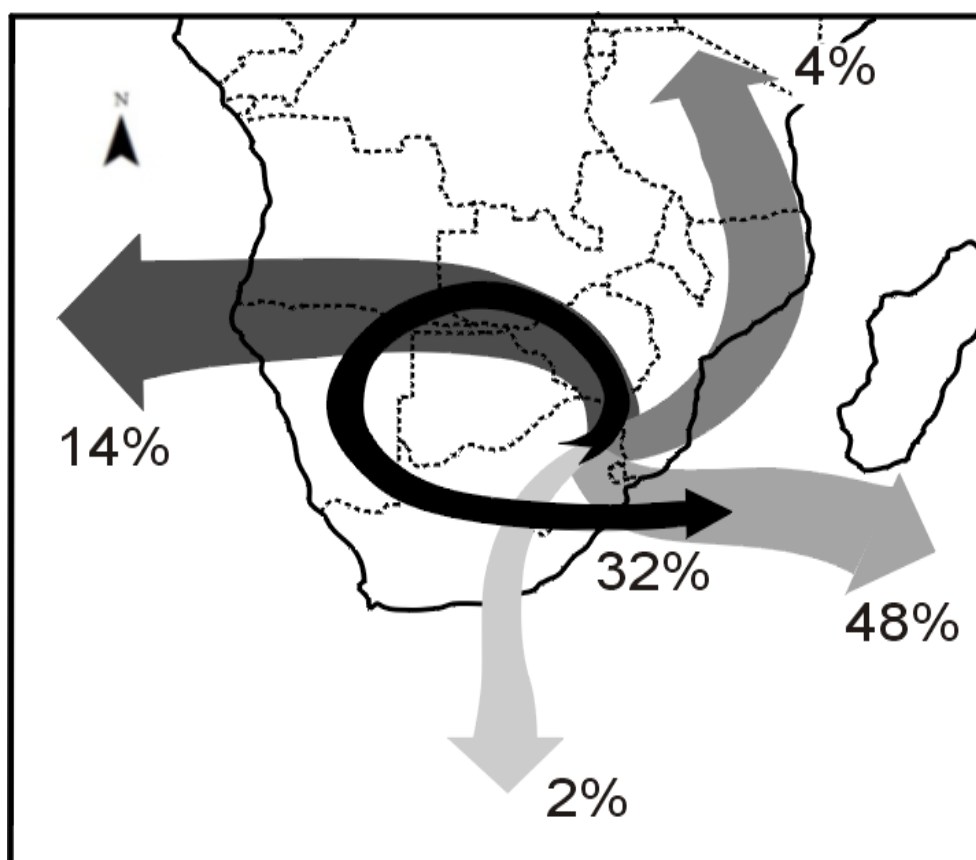
Figure 2.2: Sub-continental circulation pathways (Piketh & Prangley, 1998). The % occurrence of each circulation pattern is indicated in the figure. The arrows indicate the direction of movement from the Mpumalanga Highveld.

In the current study, the air mass history for each site for the entire sampling period was determined by calculating back trajectories with the Hybrid Single-Particle Lagrangian Integrated Trajectory

(HYSPLIT) model (Version 4.8), developed by the National Oceanic and Atmospheric Administration (NOAA) Air Resources Laboratory (ARL). This model was run with meteorological data from the Global Data Assimilation System (GDAS) archive of the National Centre for Environmental Prediction (NCEP) of the United States National Weather Service and archived by the ARL. All back trajectories were calculated for 96 hours, arriving every hour at a height of 100 m (to eliminate errors due to topographical height) throughout the entire measurement period. These individual trajectories were overlaid with a fit-for-purpose Matlab program on a map area divided into 0.2° x 0.2° grid cells. The colour of each grid cell depends on the number of trajectories passing over it, with dark red indicating the highest number of back trajectory overpasses. The overlay back trajectories obtained clearly indicate the dominant anti-cyclonic circulation pattern of air masses over the interior of South Africa. These overlay back trajectories were further used to visually indicate possible source areas affecting the sites and will be presented in the following chapter as part of the discussion (Figure 3.2).

1.2 Climate

Figure 2.3 illustrates the division of SA into four climatic regions based on the gradient in rainfall from the west towards the east as displayed in section 1.3, Figure 2.6. Areas in the west are classified as arid or semi-arid, while the east experiences tropical, wet climate conditions (Jovanovic *et al.*, 2015).
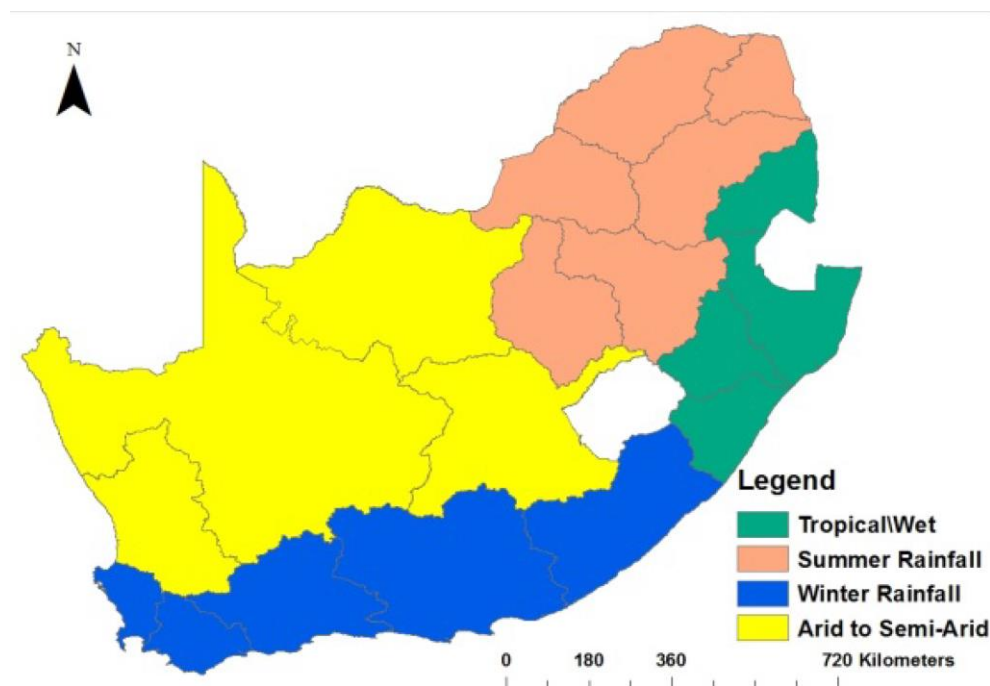
Figure 2.3: Climatic regions of South Africa based on water management areas (Jovanovic, *et al.*, 2015)

Air temperatures are typically moderate near the coastal regions of the country, while higher temperatures are experienced in the north-west (Figure 2.4) (Jovanovic *et al.*, 2015). It is estimated that South Africa will experience a general warming climate across the country with higher temperatures in sub-humid areas (Dennis & Dennis, 2012). Temperature is expected to increase with approximately 1.5°C along the coast and 2 to 3°C inland by 2050 (Mukheiber, 2008).
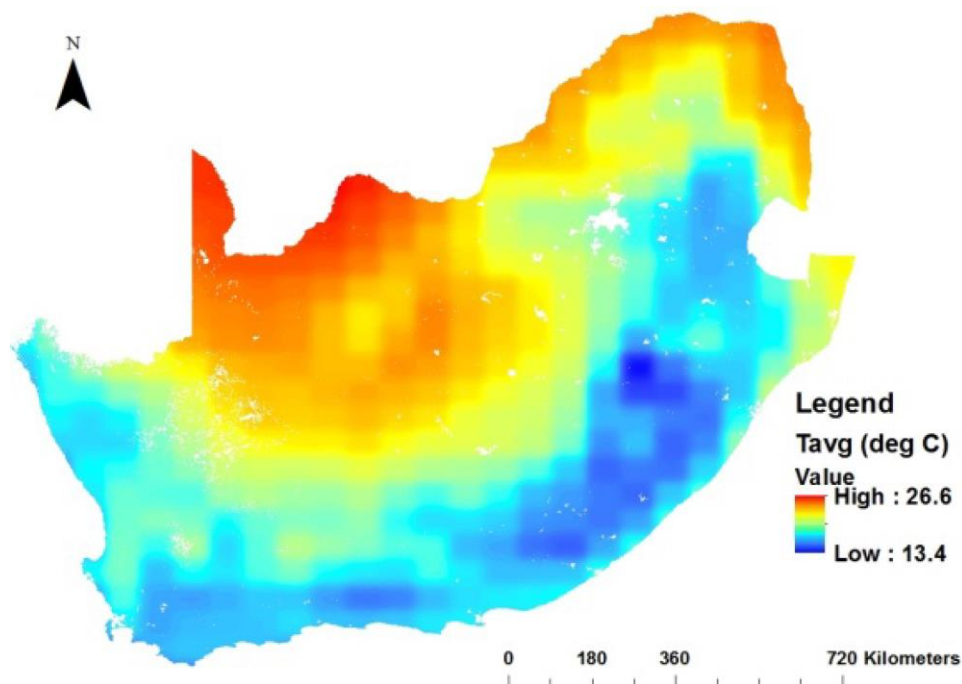
Figure 2.4: Average annual air temperature for a typical year (2009) (Jovanovic, et al., 2015)

Africa is classified as one of the more vulnerable continents with regard to climate change due to multiple stresses and low adaptive capacity. SA is a water-limited country and is situated in a region with increasing levels of water scarcity and water quality problems (Dennis & Dennis, 2012).

1.3 Rainfall

Topography (i.e. altitude) is a fixed physical parameter that exerts great influence on climate features and hydrological responses. Influences on climate include acting as a barrier to rain-bearing masses, or alternatively by forcing moist air to rise by means of orographic lifting. High altitudes together with a steep altitude gradient also cause increased thunderstorm activity and more incidences of storm flow events (Schultze, 2012). The altitude (m) of South Africa is illustrated in Figure 2.5.
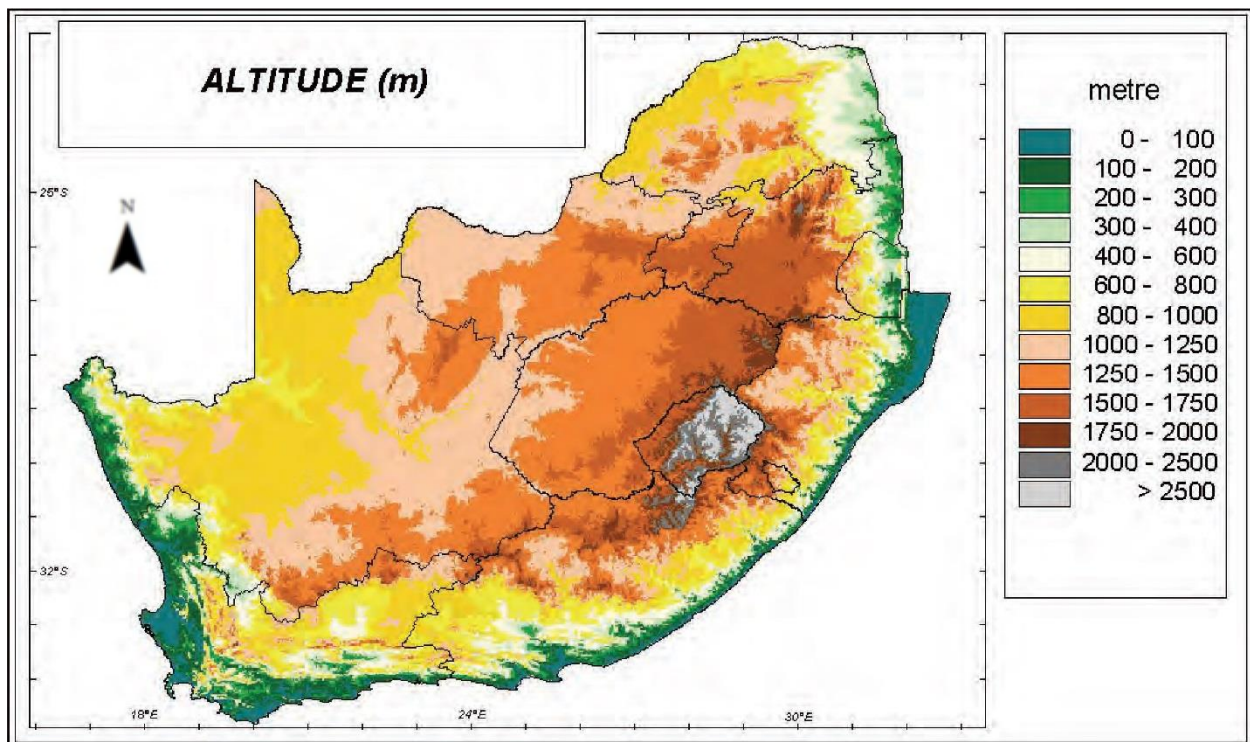
Figure 2.5: Altitude map of South Africa (Schultze, 2012)

Rainfall in South Africa is strongly seasonal, with precipitation over the central and northern parts of South Africa occurring almost exclusively during the wet season from mid-spring up to early autumn (mid-October to March), mostly in the form of convective precipitation (Hewitson & Crane, 2006; Kruger, 2006; Laakso *et al.*, 2012). The lack of precipitation and associated wet removal of pollutants during the dry period (April to mid-October), together with the additional occurrences of large-scale wild fires during the dry season and increased household combustion for space heating during the cold winter months, also leads to higher levels of most pollutant species during the dry season (refer to Chapter 4 for a detailed explanation).

The mean annual precipitation distribution over South Africa is illustrated in Figure 2.6. The mean annual precipitation decreases from the escarpment across the interior in a westerly direction (Schultze, 2012). Approximately 20% of SA receives less than 200mm rain per year, and 47% receives less than 400mm per annum. This is the result of the subtropical high pressure cells (Figure 2.1) that inhibit rainfall generation due to predominantly subsiding air. Only approximately 8% of the entire South Africa receives rainfall in excess of 800mm per annum (Lynch, 2004).

Chapter 2
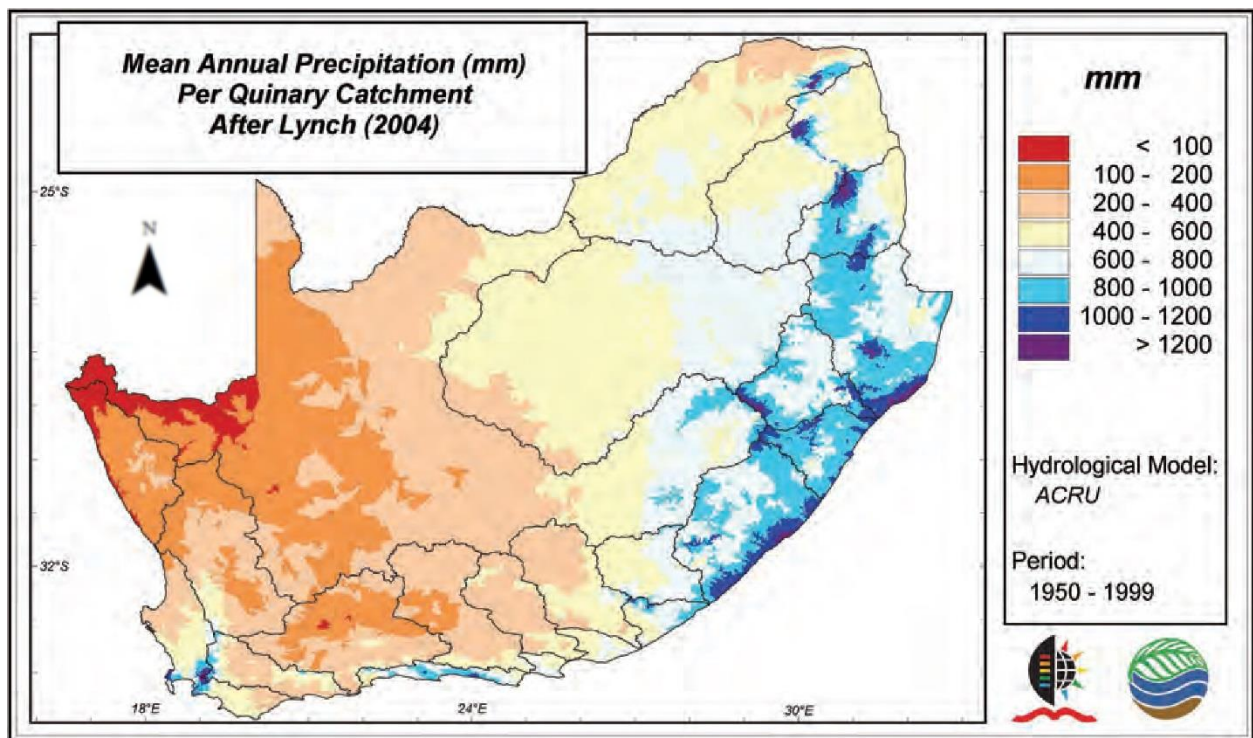
Figure 2.6: Mean annual precipitation of SA from 1950-1999 (Schultze, 2012; Lynch, 2004)

For the current study, annual precipitation typically ranged between 576 and 912 mm at AF, 818 and 1 083 mm at VT, 482 and 902 mm at LT and 475 and 786 mm at SK (2009-2013). Relatively large inter-annual rainfall variability is observed at AF and LT. Annual rainfall at SK was relatively constant, with the exception of 2013 that had higher annual rainfall compared to previous years, while the annual rainfall at VT was comparable for all five years. Changes in rainfall is represented later on in Chapter 4 (Figure 4.1).

2 Site selection and description

2.1 Selection of sites

The sites for the current study are represented within a regional context in Figure 2.7. Amersfoort (AF), Louis Trichardt (LT) and Vaal Triangle (VT) are located on the South African Highveld, while Skukuza (SK) is situated in the South African Lowveld (also refer to section 1.3, Figure 2.5). The choice of sampling sites was made after several geographical and logistical considerations, namely the availability of personnel to manage the sampling process and the transport pathways of air masses (refer to section 1.1, Figure 2.2) to name a few (Dhammapala, 1996). Site descriptions for AF, LT and SK have been described by Mphepya *et al.* (2004 and 2006) and Martins *et al.* (2007), while VT has not previously been introduced.
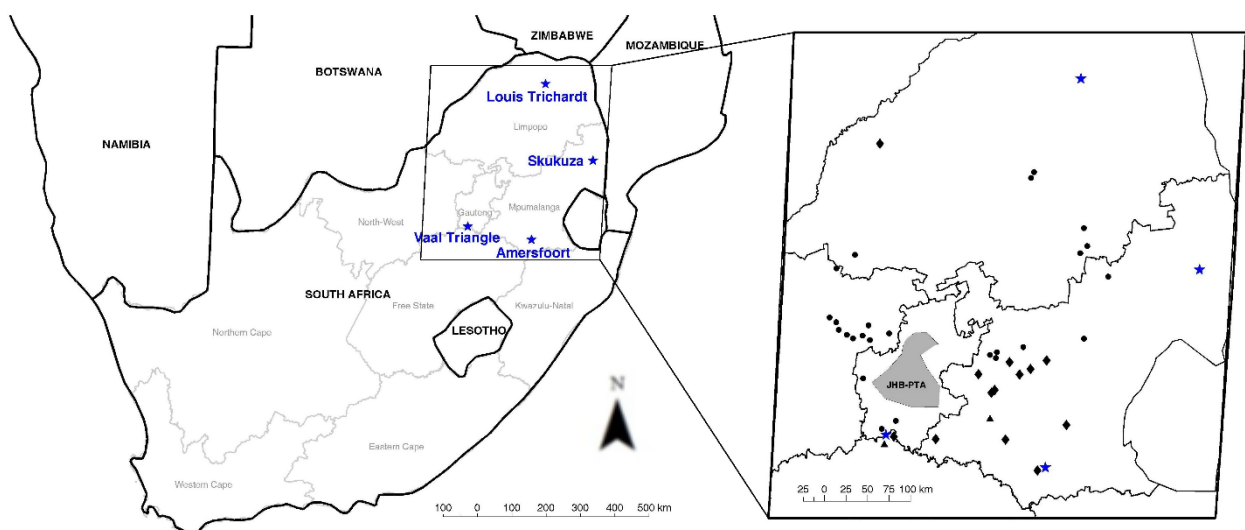
Figure 2.7: The location of the sites used in this study. The enlarged section indicates the Johannesburg-Pretoria metropolitan area with a grey shade, the sites are indicated with a blue star, petrochemical industries are indicated with a triangle, coal-fired power stations with a diamond and pyro metallurgical industries with a circle.

Furthermore, there are two types of biomes that are of interest in the current study, namely the grassland and the savannah biomes. Figure 2.8 illustrates the different biomes found in SA and also provides an indication in which biomes the sites are situated. Two types of grasses are of importance to the study sites, namely C3 and C4 type grasses. C4 grasses are those grasses that produce 4-carbon compounds as their first stable products and C3 grasses are those that produce phosphogluceric acid as the first stable product (Tieszen *et al.*, 1979).

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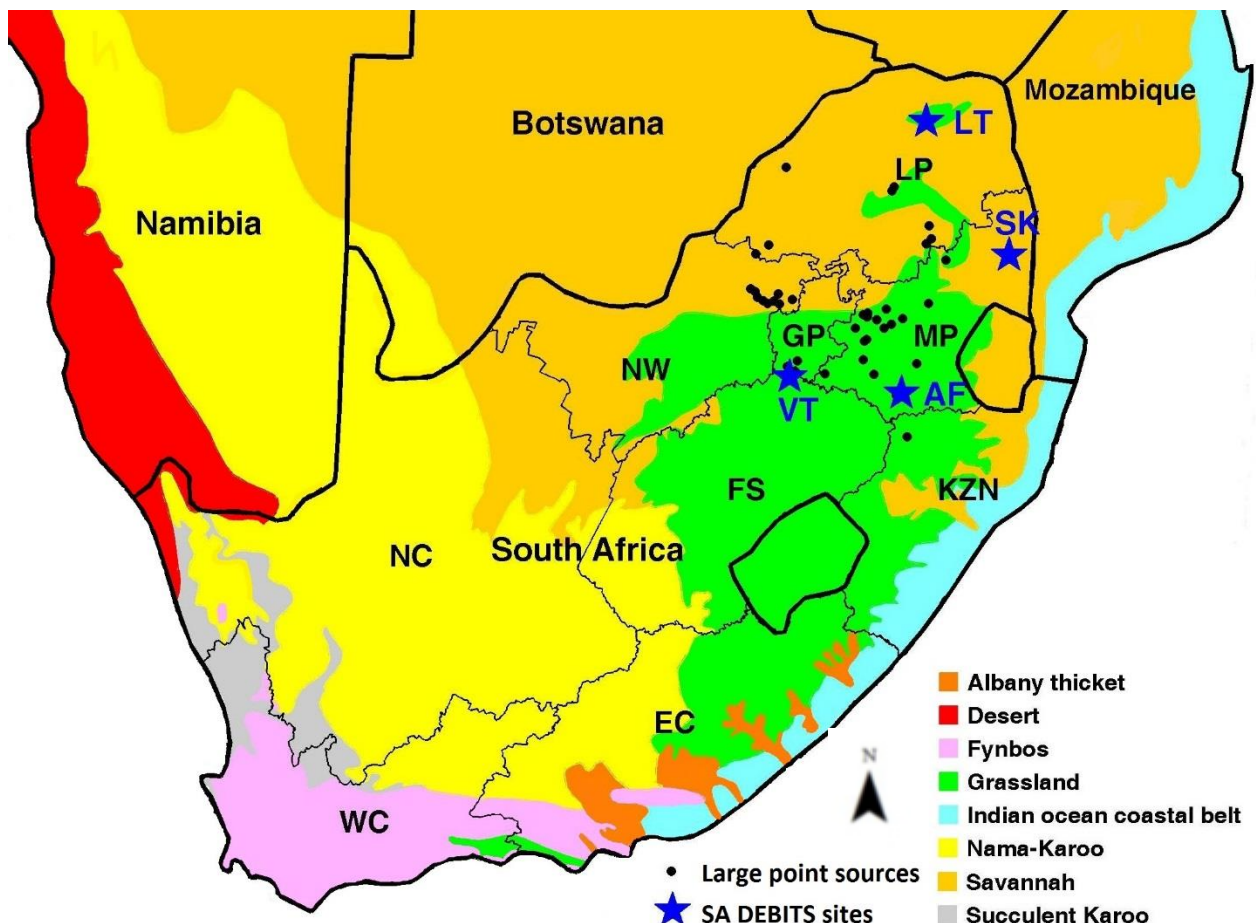
Figure 2.8: South African biomes (refer to the legend for the various types). The provincial borders are indicated with a soft line and international borders with a bold line. The SA DEBITS sites are indicated with a blue star and large pollution point sources with a black dot.

The Grassland Biome is found mainly on the high central plateau of South Africa and the inland areas of KwaZulu-Natal and the Eastern Cape. The topography is mainly flat and rolling, but includes the escarpment itself (Figure 2.5). Altitude varies from near sea level to 2 850 m above sea level. Grasslands (also known locally as Grassveld) are dominated by a single layer of grasses (Rutherford & Westfall, 1986, 1994; Mucina & Rutherford, 2006). The amount of cover depends on rainfall and the degree of grazing. Trees are less abundant, except in a few localised habitats. Geophytes (bulbs) are often abundant. Frost, fire and grazing maintain the grass dominance and prevent the establishment of trees. There are two categories of grass plants, i.e. sweet grasses have lower fibre content, maintain their nutrients in the leaves in winter and are therefore palatable to stock. Sour grasses have higher fibre content and tend to withdraw their nutrients from the leaves during winter so that they are unpalatable to stock (Rutherford & Westfall, 1986, 1994; Mucina & Rutherford, 2006). At higher rainfall and on more acidic soils, sour grasses prevail, with 625 mm per year taken as the level at which unpalatable grasses predominate. C4 grasses dominate throughout the biome, except at

the highest altitudes where C3 grasses become prominent (Rutherford & Westfall, 1986, 1994; Mucina & Rutherford, 2006).

The Savannah Biome is the largest biome in southern Africa, occupying over one-third of the area of South Africa. It is well developed over the Lowveld and Kalahari region of South Africa. It is characterised by a grassy ground layer and a distinct upper layer of woody plants (Rutherford & Westfall, 1986, 1994). Where this upper layer is near the ground, the vegetation may be referred to as Shrubveld, where it is as dense as Woodland, and the intermediate stages are locally known as Bushveld. The environmental factors delimiting the biome are complex: the altitude ranges from sea level to 2 000 m; rainfall varies from 235 to 1 000 mm per year; frost may occur from 0 to 120 days per year; and almost every major geological and soil type occurs within the biome (Rutherford & Westfall, 1986, 1994). The grass layer is dominated by C4-type grasses, which are at an advantage where the growing season is hot; however, where rainfall has a stronger winter component, C3-type grasses dominate. The shrub-tree layer may vary from 1 to 20 m in height, but in the Bushveld typically varies from 3 to 7 m. The shrub-tree element may come to dominate the vegetation in areas that are being overgrazed (Rutherford & Westfall, 1986, 1994).

2.2   Site description

The Amersfoort site is located at 27˚04'53" south and 29˚52'05" east in the south-eastern part of the Mpumalanga Province, 1 628 m above mean sea level (amsl) and situated within the grassland biome (Figure 2.8). This is approximately 200 km south-east of Johannesburg and 50 to 100 km south-east (predominantly downwind) of the major industrial activities, which also include the main centre of electric power generation in the Mpumalanga Highveld area (Figure 2.7). Amersfoort falls into a climatological transition region between the Highveld and the nearby escarpment. Prevailing winds can be expected to frequently transport pollutants from the metropolitan and industrial regions (Gauteng and Mpumalanga) towards this site. This station is representative of a site strongly influenced by industry in a semi-arid area in southern Africa.

The Louis Trichardt site is located at 22˚59'10" south and 30˚01'21" east in the Northern Province, 1 300 m amsl in the grassland biome (Figure 2.8), roughly 400 km to the north-east of Johannesburg, located in the Limpopo Province (Figure 2.7). This site is upwind of the industrialised Highveld and is mainly influenced by biomass burning from countries to the north. Winds rarely blow directly from the industrialised region towards this site. However, the site is ideally located to detect any pollution that has been recirculated within the frequently occurring sub-continental anticyclone system. There are no major cities or large towns within a 100 km radius. The area is predominantly used for

agricultural purposes, such as maize and cattle farming, and therefore it can be assumed that Louis Trichardt represents a rural site in a semi-arid region in southern Africa.

The Skukuza site is located in the south of the Kruger National Park (Lowveld), 267m above mean sea level (amsl), at 24˚59'35" south and 31˚35'02" east in the north-eastern part of the Mpumalanga Province (Figure 2.7), in the low-lying savannah region of South Africa (Figure 2.8). The Kruger National Park (KNP) is bordered by Mozambique in the east and Zimbabwe in the north. The climate is characteristic of a semi-arid savannah. During the summer months, extreme hot and dry conditions are observed over the Lowveld due to its subtropical climate and high humidity. During the winter months, the presence of anti-cyclonic conditions over the interior of South Africa results in fine and mild conditions over the region. The site is surrounded by natural bushveld, and may be influenced by the winds coming from the ocean.

The Vaal Triangle site is located within the highly industrialised Vaal Triangle area, situated within one of the pollution hotspots of the country, at 26°43'29" south and 27°53'05" east, 1320 m amsl and within the grassland biome (Figure 2.8). Numerous industrial activities influence the site, as can be seen from Figure 2.7. Another difference of the VT site in comparison to the other SA DEBITS sites, is that it is situated within an urbanised region and can therefore not be classified as a rural or background site. It is important to consider these differences in surroundings when the results for the sites are compared.

3 Gaseous sampling

3.1 Sample collection

Passive samplers have been developed and used within the IDAF network to determine atmospheric concentrations of sulphur dioxide (SO_2), nitrogen dioxide (NO_2), ammonia (NH_3), ozone (O_3) and nitric acid (HNO_3). Initiating and maintaining long-term measurement programmes with active samplers have numerous constraints, such as high financial cost, the requirement of experienced operators, the use of electricity, relatively high noise levels and the instrument requires periodic field calibration, to name a few. Although passive samplers have some negative aspects (e.g. cannot detect short-term peaks and only provide averaged value over measurement period), passive samplers overcome most of the these obstacles and are easy to deploy by site operators who are non-specialists.

Passive sampler data can be useful in providing high quality data, provided that the analyses and handling of the samplers are linked to sound operational and laboratory practices. Sound QA procedures need to be followed in order to assure accuracy and reproducibility of the data. Furthermore, passive samplers should be tested and validated against active samplers from time to time to ensure reliability. Contamination needs to be prevented at all cost during the preparation and analyses of the samplers. Lastly, the storage and transport of samplers are also very important to ensure good quality and reliability of the data generated (Pienaar, *et al.*, 2015).

3.1.1 Basic principles of passive sampling devices used

The laminar diffusion of a gaseous pollutant and the trapping thereof via absorption or chemical reaction with a sorbent medium is the basic principle of the passive sampling devices used. The shape and size of the sampler determine the sampling rate. Irrespective of the geometry of the sampler, all samplers have the same basic components. Each sampler consists of an impregnated filter/molecular sieve that adsorbs the pollutant gas and a diffusion barrier with known physical characteristics, which define an effective sampling rate (Pienaar *et al.*, 2015). Quantitative information on atmospheric concentration can only be obtained when the sampler is operated in the linear uptake range, where the uptake of the pollutant is still well below the saturation point of the sorbent medium (Figure 2.9). The sorption curve is dependent on physical parameters such as the shape and size of the sampler, the air pollutant sampled and the sorbent type (Pienaar *et al.*, 2015).
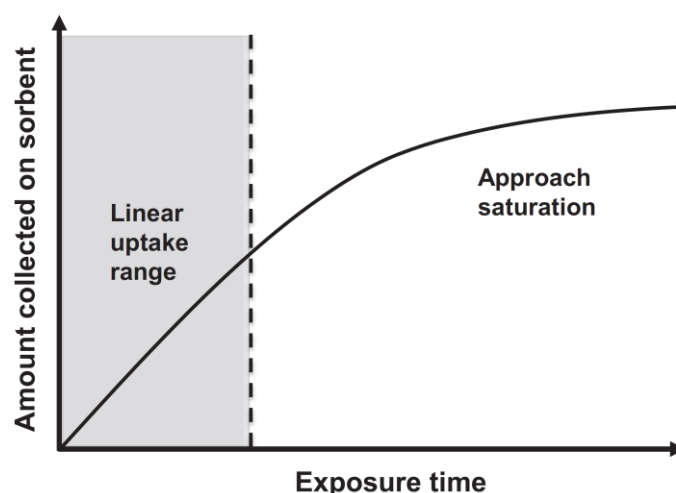
Figure 2.9: Illustration of the uptake curve for a passive diffusion sampler (Pienaar, *et al.*, 2015)

3.1.2 Description and preparation of the passive sampler

The samplers utilised in this study have been developed based on the work of Ferm (Ferm, 1991; Ferm *et al.*, 1994). A full description of how the passive samplers that were utilised in this study are prepared can be found in Dhammapala (1996). Briefly, the passive samplers work through molecular diffusion of gaseous species onto an impregnated filter within the samplers at rates controlled by their respective diffusion coefficients (Dhammapala, 1996; Josipovic, 2009; Martins *et al.*, 2007). The Ferm-type sampler is used extensively in ambient air quality studies due to its simple design and analytical laboratory requirements. It consists of a polypropylene ring with a snap-on cap at both ends, the inlet cap being removed during sampling. The impregnated filter is attached to one side of the filter. The inlet side has a 1µm PTFE filter to prevent convection by airflow and to prevent aerosols from impacting on the filter. Figure 2.10 illustrates the sampler design utilised in the IDAF network and also in this study. The impregnated filter is situated at the rear end of the sampler (Pienaar *et al.*, 2015).
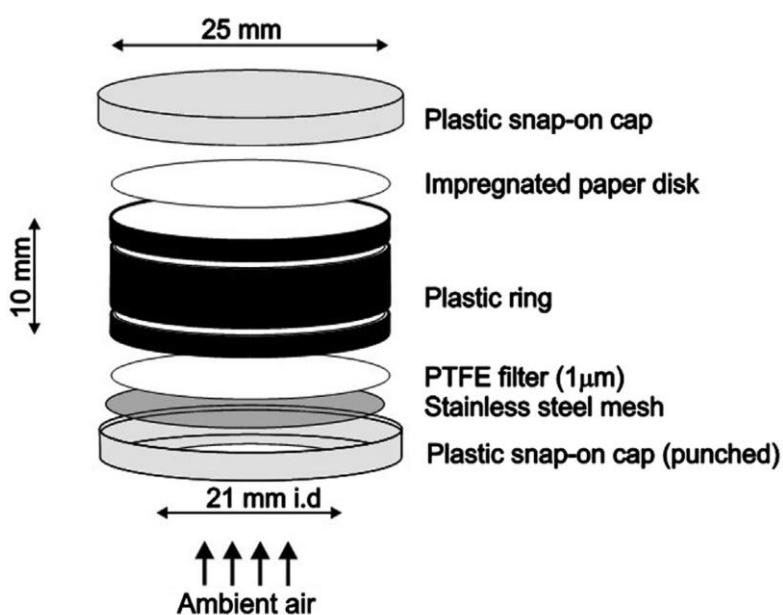
Figure 2.10: Passive sampler design employed within the IDAF network

The reactions presented in Table 2.1 illustrate the scientific basis of operation of the passive samplers (Martins, 2009; Josipovic, 2009).

Table 2.1: Chemical reactions that form the basis of operation for the passive samplers

Gas	Chemical reaction that occur on the filter	Origin of sampling method
SO_2	$2SO_2 (g) + 4OH^- + O_2^- \rightarrow 2H_2O + 2SO_4^{2-}$	IVL in Sweden
O_3	$O_3 (g) + NO_2^- \rightarrow NO_3^- + O_2$	(Koutrakis, *et al.*, 1993)
NO_2	$2NO_2 (g) + 3I^- \rightarrow 2NO_2^- + I_3^-$	IVL in Sweden
HNO_3^-	$HNO_3(g) + OH^- \rightarrow NO_3^- + H_2O$	(Ferm, 1991)
NH_3	$NH_3 (g) + H^+ \rightarrow NH_4^+$	(Ferm & Rodhe, 1997)

During this project, the samplers were prepared at the North-West University in duplicate and sealed in sterilised plastic containers for transport to the sites. A total volume of 50 mm³ of the absorbing solution was evenly pipetted over the surface area of the cellulose Whatman filter using a Gilson Pipetman micro-pipette and loaded against the snap-on cap casing at the back-end of the sampler. Table 2.2 presents the composition of the absorbing solutions used in the passive samples for the different gaseous pollutants. A more extensive description of the function of each of the reagents in the preparations mentioned above can be found in Martins (2009) and Dhammapala (1996).

Table 2.2: Preparation of passive samplers for pollutant gases (Pienaar, *et al.*, 2015)

Gas	Preparation of passive sampler filter	Reproducibility and detection limit (in brackets)
SO_2	1 g NaOH in 15 cm^3 deionised water, diluted to 100 cm^3 with methanol.	11% (0.30±0.10 µg.m^{-3})
O_3	1% (w/v) $NaNO_2$, 1% (w/v) K_2CO_3 and 2 cm^3 glycerol diluted to 100 cm^3 with a 70:30 water: methanol mixture.	
NO_2	0.88 g NaOH and 7.9 g NaI in 15 cm^3 deionised water, diluted to 100 cm^3 with methanol.	16% (0.10±0.05 µg.m^{-3})
HNO_3^-	1 g NaOH in 15 cm^3 deionised water, diluted to 100 cm^3 with methanol.	25% (0.15±0.07 µg.m^{-3})
NH_3	2 g citric acid in 15 cm^3 deionised water, diluted to 100 cm^3 with methanol.	10% (0.10±0.06 µg.m^{-3})

3.1.3   Sample collection periods and procedures

Annual averages and the associated standard deviations of NO_2, SO_2, NH_3 and O_3 for each site were calculated over an 20-year period for Louis Trichardt (1995-2014), 18 years for Amersfoort (1997-2014), 15 years for Skukuza (2000-2014) and 7 years for the Vaal Triangle (2008-2014). HNO_3 annual averages and standard deviations were determined over a 12-year period (2003-2014) for all the sites except the Vaal Triangle, where measurements only started in 2008 (2008-2014). Measurements are currently ongoing at all sites, but data after 2014 will not be reported in this study.

Samplers were sealed in air-tight plastic containers to ensure that sampling only begins when it is intended, and not before it reaches its destination or after the intended sampling period has expired. Passive samplers were exposed for one month at a height of 1.5m (chosen because it represents the height at which humans live and breathe) above ground using stands specifically designed not to cause interference with the passive sampling process. Samplers were always exposed in pairs to ensure reproducibility, accuracy and to limit data loss. After exposure, the

samplers were returned to the laboratory for analysis with the appropriate analytical methods and the concentration of the gas species determined. Each sampler was clearly marked with the necessary information (e.g. date prepared, site, species impregnated for) and sealed within a plastic container for transport. A laboratory blank was prepared for every two samplers assembled to compensate for any matrix effects, systematic errors and contaminants present in the reagents, containers, filters and laboratory during the preparation of samplers. The blanks were prepared, assembled and analysed in the same manner as the exposed samplers. All samplers that were sent to the sites had an accompanying log sheet for site operators to record the period of exposure, any environmental factors that might influence the data (e.g. fire occurrences, rainfall, hail, average daily temperature) and any possible reasons to believe that the samplers might be contaminated (e.g. insect activity on samplers during the month).

3.2 Chemical analyses

3.2.1 SO_2, O_3 and HNO_3

3.2.1.1 Apparatus and system parameters

A Dionex ICS 3000 ion chromatograph, using an ASRS 2mm column at 30°C, an isocratic setup with mobile phase at a concentration of 32 mM NaOH, and a 0.25ml/min flow rate was used. The suppressor current was set to 21 mA for O_3 analyses and 18mA for SO_2 and HNO_3. Run time per analysis was approximately 20 minutes.

3.2.1.2 Preparation of standards

- **SO_2:** A stock solution of $NaCO_3$ was prepared by dissolving 0.331 g $NaCO_3$ in 50 cm^3 deionised water. Furthermore, a stock solution of $NaSO_4$ was prepared by dissolving 0.142 g $NaSO_4$ in 1.0 dm^3 deionised water. Five standards were prepared by pipetting 0, 25, 125, 250 and 625 mm^3 of the $NaSO_4$ stock into a 25 cm^3 flask. A volume of 1.0 cm^3 of the $NaCO_3$ stock solution was added to each flask and then filled to volume with deionised water. Final concentrations were 0, 1, 5, 10 and 25 $\mu mol.dm^{-3}$ $NaSO_4$ (Martins, 2009).

- **O_3:** A stock solution of $NaNO_3$ was prepared by dissolving 85 mg $NaNO_3$ in 1.0 dm^3 deionised water. Further dilutions were made resulting in final concentrations of 0, 1, 10, 25 and 50 $\mu mol.dm^{-3}$ $NaNO_3$ (Martins, 2009).

- **HNO_3:** The same stock solution and dilutions that were prepared for O_3 were used for HNO_3.

3.2.1.3 Preparation of filters for analysis

The filters (cellulose Whatmann) were removed from the passive sampler snap-on cap and leached with 5 cm^3 deionised water (for SO_2 and HNO_3) and with 25 cm^3 deionised water (for O_3) in an ultrasonic bath for 15 minutes.

3.2.2 NO_2

3.2.2.1 Apparatus and system parameters

A Varian Cary 50 Conc. UV-vis spectrometer, with quartz cuvettes (10 mm) and set at a wavelength of 540 nm was used for the analyses of nitrite. The colour dye used was a diazotising agent consisting of 2 g sulphanilamide, 0.05 g N-1-Naphthylethylenediamine di-hydrochloride (NEDA) and 2.0 cm^3 H_3PO_4, dissolved into 250 cm^3 deionised water (Martins, 2009)

3.2.2.2 Preparation of standards

Firstly, a stock solution of $NaNO_2$ was prepared by dissolving 0.069 g $NaNO_2$ in 1.0 dm^3 deionised water. The second step was to prepare a stock solution of NaI by dissolving 0.198 g NaI in 50 cm^3 water. The standards were then prepared by adding 0, 10, 25 50 and 125 mm^3 respectively of $NaNO_2$ stock to 5 cm^3 diazotising agent and 1 cm^3 of NaI stock and diluted to a volume of 10 cm^3. Final concentrations of the standards were 0.0, 1.0, 2.5, 5.0 and 12.5 $\mu mol.dm^{-3}$ $NaNO_2$ (Martins, 2009).

3.2.2.3 Preparation of filters for analysis

The filters (cellulose Whatmann) were removed from the passive sampler snap-on cap, leached with 5 cm^3 diazotising agent and left for 15 minutes for the colour dye to develop before introducing the sample into a quartz cuvette and scanning the sample.

3.2.3 NH_3

3.2.3.1 Apparatus and system parameters

A Varian Cary 50 Conc. UV-vis spectrometer, with quartz cuvettes (10 mm) and set at a wavelength of 633 nm was used for the analysis of NH_3. The ammonium in the samples and standards was treated with a colour dye using the Indophenol-Blue method. This dye consists of a combination of two solutions, namely a hypochlorite solution (0.25 g NaOH + 20 cm^3 commercially available Javel solution with 3.5% OCl^- content), diluted to 500 cm^3 with deionised water; and a phenol-

nitroprusside solution (5 g phenol + 0.025 g Sodium nitroprusside), diluted to 500 cm^3 with deionised water (Martins, 2009).

3.2.3.2   Preparation of standards

A stock solution of di-ammonium hydrogen citrate was prepared by dissolving 0.113 g into 1 dm^3 deionised water. Standards were prepared by pipetting 0, 50, 125, 250 and 500 mm^3 stock solution into 25 cm^3 volumetric flasks. 10 cm^3 of each of the phenol-nitroprusside and hypochlorite solutions were added and standards were diluted to the appropriate volume using deionised water. The standards were left for 30 minutes for colour development (Martins, 2009).

3.2.3.3   Preparation of filters for analysis

Samplers were prepared by removing the cellulose Whatmann filters from the passive samplers and leached in 10 cm^3 of both the phenol-nitroprusside solution (added first) and the hypochlorite solution. The resulting solutions were left for 30 minutes for colour development (Martins, 2009).

3.3   Quality control/quality assurance

Quality checks on data have been performed in several inter-comparison studies over the years and are discussed in this section. These studies is good practice and recommended (Pienaar, et al., 2015) for quality assurance of passive sampling. Inter-comparison is carried out between collaborating networks as well as between different laboratories within networks. Inter-comparison with active monitor samplers is essential for the incorporation of correction factors (if necessary), especially if the pollutant of interest is measured indirectly (e.g. O_3) (Pienaar, *et al.,* 2015).

Examples of inter-comparison studies and performance testing of passive samplers conducted at the NWU:

An inter-comparison study was conducted in 1994 at Elandsfontein in the Mpumalanga Highveld at one of Eskom's monitoring sites situated within a 50 km radius of seven 4000 MW power stations. Samplers assembled by the NWU, the CSIRO in Australia and the Swedish Institute for Environmental Research - IVL were analysed and compared against those of a calibrated commercial UV Fluorescence SO_2 monitor, an UV absorption O_3 monitor and a chemiluminescence NO_2 monitor operated at the site. The reproducibility and comparability of the results were within acceptable ranges, as reported by Dhammapala (1996).

A new inter-comparison study (started early in 2007) of all countries involved in the RAPIDC programme started comparing passive samplers of the CAD, APINA and DEBITS projects. This inter-laboratory comparison, which ended in 2008, was coordinated by the National University of Singapore (NUS) and the IVL in Sweden (He, *et al.,* 2009). This inter-comparison study consisted of two phases. During phase 1, unexposed samplers were sent to NUS, where the samplers were exposed, analysed and subsequently compared to active samplers. In phase 2, samplers were exposed locally, where after samplers were analysed both at the NWU and by the NUS. The results of this study are shown in Figures 2.11 and 2.13. The passive samplers showed good correlation compared to active samplers employed at the NUS (Figures 2.11a and b, Figures 2.12a and b). The analytical methods (Figure 2.13) applied at the NWU also compared favourably with the base case analysis (NUS) chosen for this inter-comparison.
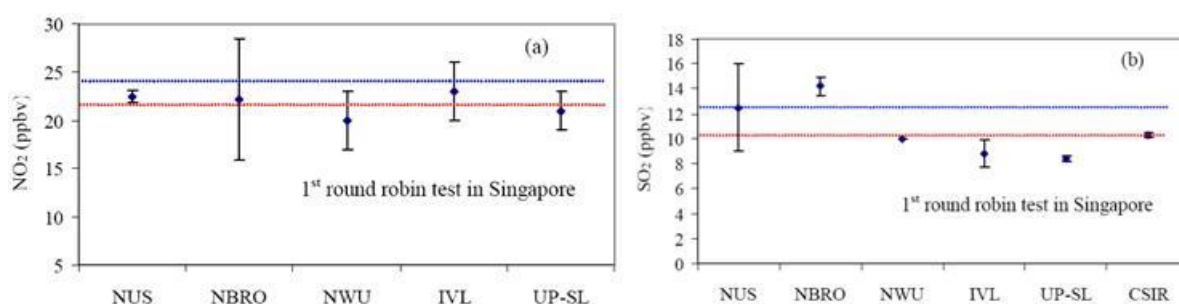
Figure 2.11: Round 1 comparing active and passive sampling conducted by the University of Singapore. The blue line represents the average of the active sampler, the red line represents the mean value of all the participants (National University of Singapore (NUS); National Building Research Organisation (NBRO), Sri Lanka; North-West University (NWU), South Africa; University of Peradeniya (UP-SL), Sri Lanka) and the error bars indicate the standard deviation based on three independent measurements.
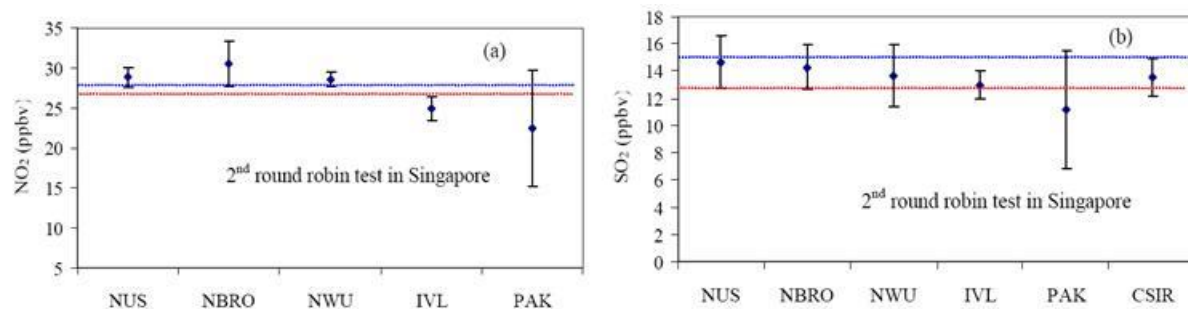
Figure 2.12: Round 2 comparing active and passive sampling conducted by the University of Singapore. The blue line represents the average of the active sampler, the red line represents the mean value of all the participants (National University of Singapore (NUS); National Building Research Organisation (NBRO), Sri Lanka; North-West University (NWU), South Africa; University of Peradeniya (UP-SL), Sri Lanka) and the error bars indicate the standard deviation based on three independent measurements.
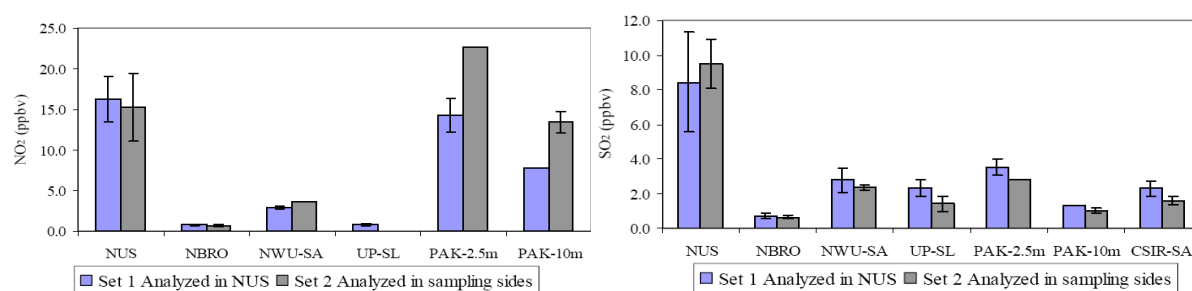
Figure 2.13: Comparison of analytical methods for NO_2 and SO_2 at the various institutions

In another comparison study (conducted in 2009), NWU passive samplers were exposed monthly for a period of six months at the NWU/University of Helsinki (UH) mobile station to determine the precision (repeatability) and accuracy (comparison with active samplers). Measurements were evaluated for SO_2, NO_2 and O_3 sampling. As an example, the correlation of SO_2 passive and active sampling is shown in Table 2.3

Table 2.3: Accuracy and precision of SO₂ passive samplers measured in 2009

Month	Passive AVG ppb	Active AVG ppb	STD	Number of outliers (95% Q-test)
March	5.5	6.2	1.2	0
April	2.9	4.1	0.5	0
May	4.5	5.9	1.4	0
June	3.2	4.0	0.7	1
July	5.8	6.3	1.4	0
August	4.4	4.7	1.0	0

4 Precipitation

4.1 Sample collection

Rainwater samples were collected on an event basis with an automated wet-only sampler (Aerochem Metrics, model 301) that exposes the collector, which is a high-density polyethylene (HDPE) bucket, only when it starts raining (Figure 2.14). The bucket is lined with a plastic bag that is replaced after each rain event. The device is equipped with a conductivity sensor that detects the onset of precipitation and activates a mechanism that opens the lid. This conductivity sensor is also heated to facilitate evaporation of the water on the sensor, thereby ensuring the closure of the lid shortly after the rain event had stopped. The advantages of automated wet-only sampling include limiting the contamination of rainwater by dust and other unwanted materials before and after the events. Furthermore, the delay in the execution of manual operation is reduced to a minimum. All samples were removed from the collectors as soon as possible, but at least within 24 hours after an event ended.
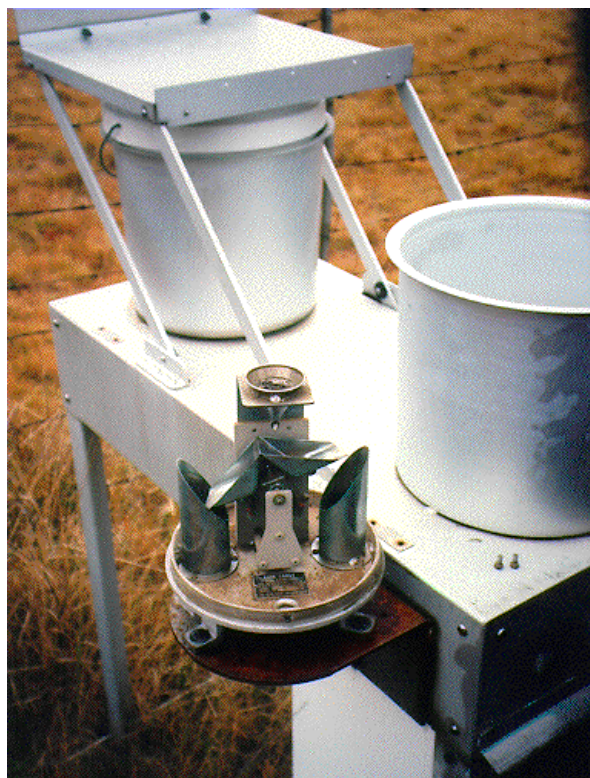
Figure 2.14: Automated wet-only sampler (Aerochem Metrics, model 301)

After wet-only collection, the precipitation was divided into two samples in polyethylene bottles. The samples were frozen at below 0°C, but above -10°C at the site by a site operator. These frozen samples were collected once a month at the sites, transported in a frozen state using a portable deep-freeze and kept in a frozen condition in the analytical laboratory until analysed. Before analysis, samples were unfrozen overnight. 25 ml of aliquots were taken for immediate conductivity and pH measurements, and the remaining sample was filtered through a 0.2μm filter in preparation for chemical analysis.

4.2   Chemical analyses

The chemical composition of rainwater samples collected at each of these sites was analysed using a Dionex ICS 3000 ion chromatograph. A five-point calibration ranging from 10 ppb to 2 ppm was compiled. Stock solutions for each ion species analysed for were obtained from Industrial Analytical and analysed from lowest to highest concentration. Analyses of the samples only commenced once the calibration curve had a relative standard deviation of 5% or less for each ionic species separately. Analyses of anions and organic acid analyses were performed with an ASRS 2mm column, using gradient automated eluent generation mode (1.5 mM up to 32 mM NaOH) and a flow of 0.25 ml/min to achieve optimal separation of the various anions. Cation analyses were conducted on a

CSRS ultra 2mm column, at a fixed eluent concentration of 25 mM methane sulfonic acid (MSA) and a flow of 0.45 ml/min. An HI 255 combined meter (Hanna Instruments) was used for pH and conductivity measurements. A three-point pH calibration procedure was followed according to the manufacturer's specifications with pH 4.01, 7.01 and 10.01 buffer solutions.

4.3   Quality control/quality assurance

The WMO Data Quality Objectives (DQOs) presented in the WMO precipitation chemistry guidance manual (WMO, 2004) were the foundation on which data quality was ensured. All collected wet deposition events were visually inspected to exclude any visible contamination, e.g. any plant materials or insects. If any contamination was observed, it was recorded and the sample was filtered through a 0.2 µm filter (Sigma Aldrich) prior to the chemical analysis. The analytical techniques, i.e. IC, pH and conductivity measurements were also verified by participating in the bi-annual inter-laboratory comparison study (LIS) organised by the WMO. In Figure 2.15, the results of the 50th LIS study in 2014 are presented (other results from the bi-annual LIS can be viewed at https://www.qasac-americas.org. – Lab ID is 700152). According to the WMO inter-comparison results, the recovery of each ion in standard samples was between 95 and 105%. Data quality was further ensured by calculating the ion difference (ID) for each sample in order to consider the ionic balance by using the following equation (WMO, 2004):

Ion difference (%) = 100 x ([CE – AE] / [CE + AE])   (1)

where AE is the sum total of the anions in $\mu eq.l^{-1}$ and CE is the sum total of the cations in $\mu eq.l^{-1}$. Acceptable limits for the ID are presented in a WMO GAW report 160 (2004) and were applied in this study. Only samples that passed these criteria were included in the study. The number of wet deposition samples collected included all the events for which rain depth was measured. All these rain events had rain depths of more than 0.2 mm. According to exposure sheets received with each of the wet deposition samples, no incidences were reported where collected wet deposition samples had to be excluded due to instrumental or operational failures during the entire sampling period. Furthermore, exposure sheets also indicated that all the wet deposition samples collected represent a single rain event and do not contain an accumulation of several rain events.
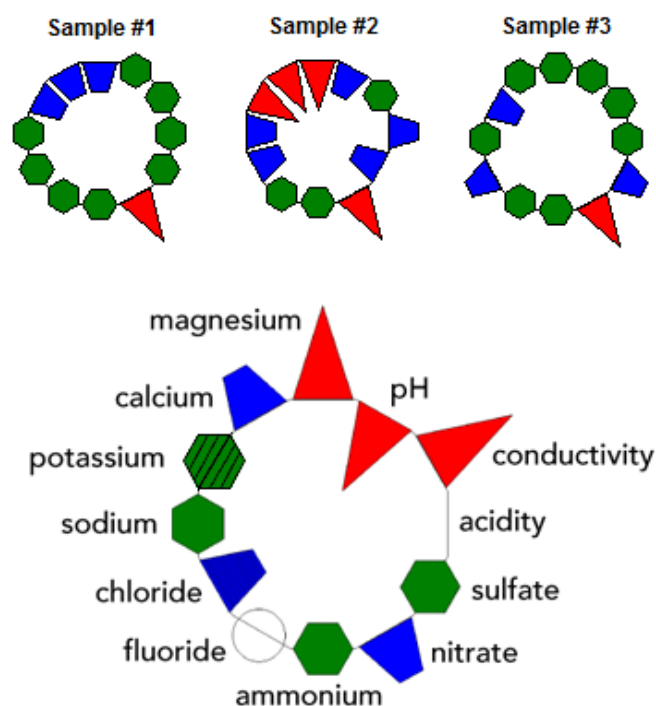
Figure 2.15: Results of the LIS 50 study in 2014 indicated by ring diagrams with a legend for the ring diagram included. The green hexagon indicate that the results are good (measurements are within the interquartile range (IQR), defined as the 25th to 75th percentile or middle half (50%) of the measurements), the blue trapezoid indicates that results are satisfactory (measurements are within the range defined by the median + IQR/1.349) and the red triangle indicates that the results are unsatisfactory (measurements are outside the range defined by the median + IQR/1.349). IQR/1.349 is the non-parametric estimate of the standard deviation, sometimes called the pseudo-standard deviation (QA/SAC-Americas, 2014).

5   Conclusion

This chapter presented the meteorology and climatology of South Africa and its influence on the selected sites for this study. Other geographical factors that might influence measurements at these sites were also briefly discussed. Furthermore, this chapter described the quality control and quality assurance protocols that were used to ensure data integrity as well as quality. In the following chapters, the results obtained for gaseous and wet sampling will be discussed in more detail.

Chapter 3: Gaseous measurements and dry deposition estimations by using passive sampling

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In this chapter, a brief introduction to trace gases is provided, followed by a discussion of passive sampling results at Louis Trichardt (LT) (1995-2014), Amersfoort (AF) (1997-2014), Skukuza (SK) (2000-2014) and the Vaal Triangle (VT) (2008-2014). Results from the current study were also placed into context with other studies done locally, on the African continent and globally. Furthermore, inter-annual variations, deposition estimates and seasonal variations are discussed.

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1   Introduction

1.1   Historical perspective on trace gases and their importance

The atmosphere's composition is approximately 78% nitrogen by volume, 21% oxygen and 0.9% argon. The concentrations of these gases have remained remarkably constant over centuries. The remainder of the atmosphere is a complex mixture consisting of numerous gaseous species in trace amounts (together, comprising less than 1% of the atmosphere), that is highly variable due to both natural and anthropogenic activities (Laj *et al.*, 2009). These species are of great importance due to their reactivity in the atmosphere, as well as the role they play in atmospheric chemistry and the earth's radiative budget (Seinfeld & Pandis, 2006; Wallace & Hobbs, 2006). All gaseous species have a specific function in biological cycles and within the atmosphere (Laj *et al.*, 2009). Atmospheric chemistry determines the natural and anthropogenic makeup and abundance of pollutant species such as aerosols and gases on a regional scale (Isaksen *et al.*, 2009).

Atmospheric chemistry initially focused on determining the composition of the atmosphere. When air pollution became a problem associated with health and environmental impacts, the focus shifted towards the identification, quantification, sources, properties and impacts of the numerous chemical species known to be present in the atmosphere (Seinfeld & Pandis, 2006). As more studies focused on the impacts of air pollutant species, the focus started shifting towards acid rain and the impacts thereof, which also led to studies regarding atmospheric transport and secondary transformation processes that occur. The more recent studies have focused on the effects that trace chemical species have on the earth's climate and radiative budget, as well as on environmental impacts such

as deposition that can lead to the acidification and eutrophication of ecosystems (Wallace & Hobbs, 2006; Vet *et al.*, 2014).

It is important to monitor the impact of deposited pollutants on terrestrial and aquatic ecosystems to help with scientific assessments needed for environmental policies (Vet *et al.*, 2014). Ecosystems have a natural capacity to assimilate acid deposition. This buffering capacity needs to be well understood in order to ensure that no long-term irreversible ecological impacts arise from permitted emissions. Impacts of pollutants on an ecosystem need to be evaluated on a region-specific basis, since the effects and sensitivity of a terrestrial ecosystem are very specific (Bleeker *et al.,* 2011). Deposition rates also provide valuable information on pollution loads in the atmosphere, and to what extent human activities have altered atmospheric chemistry.

1.2 Health and environmental impacts

It is by this time well known that the release of atmospheric acidifying compounds, such as nitrogen and sulphur compounds, can cause adverse human health effects, impacts on aquatic ecosystems and accompanying forest decline (Möller, 1999), acid rain and acidification of the environment (Gorham, 1998), damage to buildings and sculptures (Ozga *et al.*, 2011; Dolske, 1995), eutrophication (Adon *et al.*, 2010; 2013; Martins *et al.*, 2007), soil nutrient depletion, as well as loss of animal and plant diversity and tropospheric ozone depletion (Staelens *et al.*, 2012).

The cause of air pollution is more often than not associated with anthropogenic disturbances and emissions that are vast, especially in urban and industrialised regions of the globe (Wallace & Hobbs, 2006). Air pollution represents the biggest environmental risk to human health (WHO, 2016). In 2012, one out of every nine premature deaths was the result of air pollution-related conditions. Of these, approximately 3 million premature deaths are attributable solely to ambient (outdoor) air pollution. Air pollution affects all regions, settings, socio-economic groups and age groups (WHO, 2016).

1.3 Biogeochemical cycles

Geochemical cycling can be defined as the continuous cycling of chemical species through the global environment via various reservoirs, because chemical species cannot accumulate indefinitely in any of these reservoirs under steady-state conditions. Reservoirs for chemical species are the atmosphere, hydrosphere, cryosphere, biosphere and the solid earth (Brasseur *et al.*, 1999; Wallace & Hobbs, 2006).

Factors that influence the biogeochemical cycles of gaseous species include resource use, industry, agricultural activity, deforestation, biomass burning, energy production and high population density. Due to the complexity of these biogeochemical cycles, many aspects thereof are poorly understood and therefore quantities contributed by sources or removed by sinks can currently only be considered as rough estimations (Brasseur *et al.*, 1999; Wallace & Hobbs, 2006). Consequently, the quantification of sources and sinks, by for example conducting deposition studies, can provide additional insight into these complex biogeochemical cycles.

1.3.1 The nitrogen cycle

Atmospheric nitrogen consists almost entirely out of relatively inert N_2 (99.99%) and the remainder almost entirely out of N_2O (approximately 99% of the remainder). Therefore, all non-N_2 nitrogen-containing species in the atmosphere are in trace amounts. Of all the nitrogen-containing gaseous species, NH_3 is the only basic gas and it is therefore solely responsible for neutralising acidic gases such as SO_2 and NO_2 (Fowler *et al.*, 2015; Wallace & Hobbs, 2006).

There are two processes, namely *fixation* and *nitrification/denitrification,* which regulate the geochemical cycling of nitrogen. All of the nitrogen-containing gases in the atmosphere are involved in these two biological processes (Fowler *et al.*, 2015; Wallace & Hobbs, 2006). *Fixation* refers to the uptake of nitrogen from the atmosphere into ecosystems. Enzymes transform the nitrogen into NH_3, which can then be absorbed by plants and microorganisms. NH_3 undergoes *nitrification* to produce nitrite (NO_2^-) and nitrate (NO_3^-). Nitrate is absorbed by plants through their roots (Wallace & Hobbs, 2006). *Denitrification* usually occurs under anaerobic conditions and it is the process where nitrate is converted through bacterial reduction to nitrite and eventually N_2 and N_2O and released back to the atmosphere (Fowler *et al.*, 2015).

The main sources that influence the nitrogen cycle include terrestrial and marine emissions, biomass burning, fossil fuel combustion, lightning, decomposition of organic matter and animal urea. Sinks include wet deposition, dry deposition, chemical breakdown and transformation (Fowler *et al.*, 2015).

1.3.2 The sulphur cycle

Sulphur in the *ambient background* atmosphere is mainly in the reduced state; the most important gases being H_2S, DMS, COS and CS_2. These reduced gases are oxidised to SO_2. Since SO_2 is one of the main pollutants emitted by fossil fuel combustion, SO_2 concentrations are usually higher than that of the reduced sulphur-containing species in anthropogenically polluted environments. Approximately

65% of SO_2 is further oxidised to SO_4^{2-}, which is removed through wet deposition or dry aerosol deposition. The remaining SO_2 is removed through dry gaseous deposition. (Charlson *et al.*, 2000; Wallace & Hobbs, 2006).

The main sources that influence the amount of sulphur in the atmosphere include biogenic reactions from phytoplankton in the ocean (source of DMS, COS and CS_2), anthropogenic emissions such as fossil fuel combustion (source of SO_2 and in some cases H_2S), volcanoes (source of SO_2 and SO_4^{2-}), soil/marshland emissions (source of H_2S, COS and CS_2) and biomass burning (source of SO_2) (Charlson *et al.*, 2000; Wallace & Hobbs, 2006).

1.4 Tropospheric chemistry of important trace gases

1.4.1 OH radical

Although research on the OH radical (HO$^\bullet$) is not a part of the current study, it is necessary to discuss it briefly due to the important role it plays in tropospheric chemistry. HO$^\bullet$ is highly reactive to both organic and inorganic compounds. Atmospheric compounds that do not react, or react very slowly with HO$^\bullet$ (e.g. chlorofluoro-carbons that are commonly known as CFCs) are unlikely to react with any other reactive intermediates in the troposphere. HO$^\bullet$ is produced when O_3 molecules are decomposed by solar UV radiation into molecular oxygen and a chemically excited oxygen atom (Connell, 2005; Wallace & Hobbs, 2006).

$$O_3 \ + \ \hbar\nu \ \rightarrow \ O_2 \ + \ O^* \tag{3.1}$$

Most of the O^* recombines with O_2 to produce O_3 (a null cycle), but a small portion of the O^* atoms react with water vapour molecules and produce OH radicals (Connell, 2005).

$$O^* + \ H_2O \rightarrow 2OH \tag{3.2}$$

HO$^\bullet$ can also be produced from the photolysis of nitrous acid (HONO) or hydrogen peroxide (H_2O_2), as well as the reaction of hydroperoxy radicals (HO$_2^\bullet$) with nitric oxide (NO) (Connell, 2005).

HO$^\bullet$ is extremely reactive with most gases that contain H, N, O, S, C or halogens (except CFC and related compounds). HO$^\bullet$ is removed predominantly through the oxidation reactions of CO and methane. Because both the production of ozone and the sinks for OH have increased over the past decades, it is not certain whether the concentrations of HO$^\bullet$ have changed over the past decades (Wallace & Hobbs, 2006).

Chapter 3

1.4.2 SO$_2$

The approximate lifetime of SO$_2$ depends on the atmospheric composition and meteorology, i.e.the lifetime is 1.8 days for SO$_2$ and 5.8 days for sulfate in a normal year (Chin, *et al.,* 2000). SO$_2$ exposure over longer time periods can cause health effects such as bronchitis (Kampa & Castanas, 2008). A combination of SO$_2$ and hydrocarbons (found in coal/soot) and high levels of humidity produce an acidic and reductive atmosphere (Van Loon & Duffy, 2005). The carbon surfaces act as nuclei for water condensation, leading to the formation of smog, which is both a visual impairment, as well as an irritant to airways (Van Loon & Duffy, 2005). A 24h (short-term) exposure limit of 125 µg.m^{-3} for SO$_2$ is recommended by the WHO, while annual long-term exposure should be less than 50 µg.m^{-3} (Brimblecombe, 1996). The South African National Ambient Air Quality Standard for SO$_2$ is represented in the following table:

Table 3.1: National Ambient Air Quality Standard limits for SO$_2$ (Government Gazette, 24 December 2009)

Averaging period	Concentration	Frequency of exceedance of the Air Quality Standards allowed over the specified averaging period
10 minutes	500 µg/m^3 (191 ppb)	526
1 hour	350 µg/m^3 (134 ppb)	88
24 hours	125 µg/m^3 (48 ppb)	4
1 year	50 µg/m^3 (19 ppb)	0

Anthropogenic emissions of SO$_2$ account for approximately 25% of the total sulphur flux into the atmosphere, and more than 50% of emitted SO$_2$ into the atmosphere are from anthropogenic sources (Bates *et al*., 1992; Pienaar & Sandham, September 1995). Anthropogenic emission sources of SO$_2$ in South Africa (SA) are primarily from fossil fuel combustion and coal-fired power stations, but also include smelters and other industrial processes (e.g. petrochemical plants, metallurgical industries, mining activities, brick works, steel works and fertiliser plants).

The principal natural sources of SO_2 in the atmosphere are the oxidation of DMS (emitted from biological reactions in the oceans) and H_2S (sources include oceans, volcanoes, marshlands and soil) (Bates *et al.*, 1992). Natural sources of SO_2 also include the decomposition of organic matter, the redox reactions of sulphide and sulphate (found in the aquatic and terrestrial environment), sea spray (Van Loon & Duffy, 2005), volcanoes and biomass burning (Bates *et al.*, 1992; Wallace & Hobbs, 2006).

SO_2 in the atmosphere can be oxidised to sulphuric acid or sulphate that is readily deposited dry as aerosols, or wet as part of cloud droplets (Kellogg *et al.*, 1972).

1.4.3 NO_2

Nitrogen oxides (NO_x) are air pollutants that play an essential role in atmospheric chemistry, since they act as precursors for tropospheric ozone and secondary aerosol formation (Jacob *et al.*, 1996; Seinfeld & Pandis, 2006). The primary emission form of NO_x in the atmosphere is NO, constituting approximately 95% of the total NO_x emissions. However, the ratio of $NO:NO_2$ differs depending on the source (ISO 10849, January 1994). The main anthropogenic sources of NO_x include coal-fired power stations, metallurgical smelters, mining and petrochemical industries, combustion in informal settlements, traffic and other combustion processes. Natural sources include lightning, biomass burning (which can also be anthropogenic) and soil denitrification (Seinfeld & Pandis, 1998; Van Loon & Duffy, 2005).

NO_x has a relatively short lifetime in the lower troposphere due to its extreme reactivity (lifetime ranges from a few hours near surface, up to a few weeks in the upper troposphere). The lifetime is affected by meteorological conditions, e.g. windy vs. calm conditions, and is typically shorter during the summer (Liu *et al.*, 2016). The chemistry of nitrogen compounds is complicated and numerous different mechanisms of transformation and deposition exist (Wallace & Hobbs, 2006; Dhammapala, 1996).

Although NO_x is primarily emitted as NO, during daytime it rapidly reaches equilibrium with NO_2 (Bradshaw *et al.,* 2000):

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{3.3}$$

$$NO_2 + O_2 + M + ℏv \rightarrow NO + O_3 + M \tag{3.4}$$

At night time, NO_2 is the predominant form of NO_x, under natural background conditions, since O_3 production does not occur then. NO_x is primarily removed by the hydroxyl radical in the daytime through the following equation (Wallace & Hobbs, 2006):

$$NO_2 + OH + M \rightarrow HNO_3 + M \tag{3.5}$$

NO_2 is an irritant gas that is absorbed by the mucous membrane of the respiratory tract. Exposure to NO_2 pollution is linked to increased susceptibility to respiratory infections, increased airway resistance in asthmatics and reduced pulmonary function nitrogen (Seinfeld & Pandis, 2006; Brasseur *et al.*, 1999). However, NO_2 is also an important source of nutrients for living organisms that has the ability to fixate nitrogen (Seinfeld & Pandis, 2006; Brasseur *et al.*, 1999). However, the global nitrogen cycle is adversely affected by human activities (Delon *et al.*, 2010), specifically by NO/NO_2 anthropogenic emissions and pollution on a global scale. NO_2 also has the ability to absorb radiation over the entire UV/VIS spectrum, and from there its significance in O_3 formation

The South African National Ambient Air Quality Standard limits for NO_2 are represented in the following table:

Table 3.2: National Ambient Air Quality Standard for NO_2 (Government Gazette, 24 December 2009)

Averaging period	Concentration	Frequency of exceedance of the Air Quality Standards allowed over the specified averaging period
1 hour	200 µg/m^3 (106 ppb)	88
1 year	40 µg/m^3 (21 ppb)	0

1.4.4 NH$_3$

Ammonia (NH$_3$), the third most abundant nitrogen compound in the atmosphere (after N$_2$ and N$_2$O), is the primary alkaline gas of the atmosphere (Behera *et al*., 2013). It has an atmospheric lifetime of less than 10 days and can be deposited by either wet or dry deposition (gaseous, or as part of aerosols). The deposited species serve as an important source of nutrients to the biosphere (Brasseur *et al.*, 1999; Seinfeld & Pandis, 2006).

Numerous natural and anthropogenic sources exist for NH$_3$, such as the decomposition of animal urine or excrement, soil emissions, biomass burning, production of fertilisers, paper manufacturing, water purification plants, petroleum industries, coal and oil combustion, household combustion and organic decomposition (Van Loon & Duffy, 2005; Brasseur *et al.*, 1999; Dhammapala, 1996).

Ammonia neutralises acids produced by SO$_x$ and NO$_x$ and almost all emitted ammonia are returned to the surface through deposition (Behera *et al*., 2013; Adon *et al.*, 2010).

1.4.5 HNO$_3$

HNO$_3$ plays an important role in the acidification of the environment. It also helps to control levels of photo-oxidants in the atmosphere, since it is a sink for NO$_2$ that could otherwise have been consumed for O$_3$ and subsequent HO$^{\bullet}$ formation. Therefore, it is critical to measure levels of HNO$_3$ in the atmosphere (Adon *et al.*, 2010).

One of the removal processes of NO$_x$ is the formation of nitric acid (HNO$_3$). The reaction of NO$_x$ with HO$^{\bullet}$ leads to the formation of HNO$_3$ as an oxidation product. The reaction occurs by any of three major pathways, namely gas phase oxidation, aqueous phase oxidation or aerosol formation (Brasseur *et al.*, 1999; Campbell, 1997). These are the only sources of HNO$_3$ in the atmosphere (Seinfeld & Pandis, 2006; Brasseur *et al.*, 1999).

Nitric acid has very short residence times in the lower troposphere (typically less than one day) (Seinfeld & Pandis, 2006; Brasseur *et al.*, 1999). It is easily removed from the atmosphere through both wet and dry deposition, and nitric acid is an extremely water-soluble atmospheric gaseous species, with a Henry's law constant of 2.1 x 105 m.atm^{-1} at 298 K.

Chapter 3

1.4.6 O_3

Tropospheric ozone (O_3) is known as the third most important greenhouse gas and additionally causes numerous environmental concerns due to impacts on human health (respiratory illness and premature deaths) (Monks *et al.*, 2009), crops and other vegetation due to its highly phytotoxic nature, and forest ecosystems (Simpson *et al.*, 2014; Adon *et al.*, 2010; Monks *et al.*, 2009) by reducing photosynthesis and plant growth (Monks *et al.*, 2009). Boundary layer tropospheric O_3 has a relatively short residence time in the atmosphere of approximately one day, due to rapid dry deposition and consumption by reactions wherein it participates (Fowler *et al.*, 2009).

The production, as well as removal, of O_3 is largely dependent on and determined by the concentrations of NO_x in the troposphere (Seinfeld & Pandis, 2006). Production of tropospheric O_3 occurs during the photolysis of NO_2. Furthermore, O_3 levels increase when ambient levels of precursor gases such as CO, VOCs and CH_4 increase (Seinfeld & Pandis, 2006).

Ozone is an almost direct indication of the oxidative potential of the atmosphere, being directly or indirectly involved in numerous reactions with trace species. Ozone has both heating and cooling effects in the atmosphere as greenhouse gas and, for example, through impacts on aerosol radiation (Simpson *et al.*, 2014). The South African National Ambient Air Quality Standard for O_3 is represented in Table 3.3:

Table 3.3: National Ambient Air Quality Standard for O_3 (Government Gazette, 24 December 2009)

Averaging period	Concentration	Frequency of exceedance of the Air Quality Standards allowed over the specified averaging period
8 hours (running)	120 µg/m^3 (61 ppb)	11

In contrast to its negative tropospheric impacts, stratospheric O_3 is very beneficial, since O_3 is the only major trace gas that has the ability to absorb UV radiation from the sun (240-290 nm) almost completely. The stratosphere contains approximately 90% of the total O_3 of the planet and is responsible for shielding the earth's surface from inbound radiation (Seinfeld & Pandis, 2006).

Chapter 3

1.5 Importance of trace gas measurement studies from a South African perspective

South Africa is regarded as an important source region of atmospheric pollutants – e.g. a very prominent NO_2 hotspot can be observed via satellite over the South African Mpumalanga Highveld, which is regarded as one of the top five NO_2 emission hotspots on a global scale (Laakso *et al.*, 2012; Lourens *et al.*, 2012; Venter *et al.*, 2012). Industries on the Mpumalanga Highveld emit large quantities of NO_x and SO_2, as well as other gaseous species from various anthropogenic sources, including power generation, petrochemical, metallurgical, ore smelting, coal mining and combustion (Josipovic, 2009; Collet *et al.*, 2010). The Highveld produces an estimated total of 90% of the emitted industrial NO_x in South Africa, with nitrogen emissions totalling an estimated 420 kt/year of nitrogen (around 1.6% of the total global emissions) (Lourens *et al.*, 2012) and South Africa is regarded as the 9th largest atmospheric S-emitting country (Stern, 2006). Furthermore, biomass burning plumes from this area are known to affect Australia and South America (Wenig *et al.*, 2003). South Africa is also regarded as the economical hub of southern Africa.

1.5.1 Previous studies in South Africa

Numerous studies have been conducted in South Africa to investigate certain aspects of air pollution in this country. South African air quality legislature makes provision for the identification of air pollution priority areas – areas where ambient air quality standards are frequently exceeded. The Vaal Triangle (VT) site of this study is situated within the Vaal Triangle Airshed Priority Area (VTAPA), while Amersfoort (AF) is situated within the Mpumalanga Highveld Priority Area (HPA). Some of the studies conducted on air pollution in SA include the characterisation studies of trace pollutants in and around the Mpumalanga Highveld or close to point sources (e.g. Lourens *et al.*, 2012; Collet *et al.*, 2010; Josipovic, 2009; Flemming & van der Merwe, 2004; Swap *et al.*, 2003; Turner *et al.*, 1996; Rorich & Galpin, 1998), transport of air pollutants has been investigated (e.g. Wenig *et al.*, 2003; Freiman & Piketh, 2003; Piketh, 2000; Galphin & Turner, 1999; Zunckel *et al.*, 1999; Turner *et al.*, 1996; Garstang *et al.*, 1996; Bluff *et al.*, 1991; Snyman *et al.*, 1991), deposition rates for both wet and dry deposition were investigated (e.g. Mphepya, 2002; Fourie, 2006; Zunckel *et al.*, 2000), new particle formation at a clean background site was investigated (e.g. Gierens *et al.*, 2013; Vakkari *et al.*, 2011; Laakso *et al.*, 2008) and also compared to an industrially impacted site situated within the bushveld igneous complex of South Africa (Venter *et al.*, 2012; Laakso *et al.*, 2012). Characterisation of source plumes was also done using a mobile air quality measurement station (e.g. Beukes *et al.*, 2013). Short periods of intensive research in the form of campaigns was also conducted in South

Africa during the SAFARI 1992 and SAFARI 2000 campaigns (e.g. Swap *et al.*, 2003; Ross *et al.*, 2003; Eck *et al.*, 2003) and also on a long-term basis by the South African Weather Service and NOAA-ESRL as part of the Global Atmospheric Watch programme at the station in Cape Point (e.g. Brunke *et al.*, 2010).

1.5.2 Current study

The current study focuses on two aspects. Firstly, it focused on the long-term measurement of the concentrations and deposition of chemical species in the atmosphere at the selected sites with the aim to evaluate long-term and seasonal trends; and secondly, calculated deposition estimates are evaluated and discussed.

Operating a long-term monitoring network, especially in a remote rural area, is difficult (e.g. competent personnel, availability of infrastructure, site maintenance, accessibility, running cost, etc.) (Carmichael *et al.*, 2003). Passive sampling offers a cost-effective, easy-to-operate system that can be implemented and recycled for use. Passive samplers can monitor many key pollutant species, including inorganic gases (e.g. SO_2, NO_2, NH_3, HNO_2, O_3), organic gases (e.g. benzene, toluene, ethyl benzene, xylene), as well as volatile and semi-volatile organic compounds (e.g. alkyl benzenes, aromatics, polychlorinated biphenyls, ketones, aldehydes, hydrocarbons) (Pienaar *et al.*, 2015). The samplers are small, lightweight, operate silently, do not require field calibration or maintenance or power supply, and can easily be deployed by a person who is not a specialist in the subject. Therefore, the samplers are ideal to employ at various sites over a long time period (Pienaar *et al.*, 2015; Adon *et al.*, 2010; Josipovic, 2009; Martins *et al.*, 2007; Dhammapala, 1996).

2 Calculations

Apart from the quality control/quality assurance measures that were described in Chapter 2, the gaseous datasets were subjected to two consecutive Q-tests with 95% confidence intervals (Rorabacher, 1991) to ensure that no outliers were used in the interpretation of the results. The first Q-test was conducted within each year (e.g. annual average), to ensure that a single monthly value did not bias the annual average that was determined. The second Q-test was performed within each month (e.g. monthly average), comparing all the years' data to ensure that a single month in a specific year did not bias the seasonal patterns that were deduced. Values that were flagged were not included in the results that are discussed in this section, unless a logical reason exists for it to be included (such as a month with an abnormal amount of rainfall, unusually high or low temperatures or large biomass burning incidents).

The deposition velocities used to calculate the deposition estimates are presented in Table 3.4. A more detailed description of each site, as well as a short discussion on the typical vegetation of the area was provided in Chapter 2. The values presented in Table 3.4 are the best estimates from a recent DEBITS publication for dry deposition in Africa (Adon *et al.,* 2013) and should be viewed **only as reasonable estimates**. The reason for choosing to evaluate all sites using the same deposition velocities was to ensure that all sites are comparable by using the same source with the same limitations applied to all parameters. Although there are deposition velocity values available that were calculated using the inferential modelling technique for some of the gaseous species at Amersfoort, Louis Trichardt (LT) and Skukuza (SK) (Martins, 2009), these values were not used in the calculations since such values are not available for all sites and for all the species investigated in this study. In order to accurately determine deposition values at a specific site, real time meteorological data and high resolution gaseous measurements are needed and none of these were available at the remote monitoring sites used in this study. Monthly mean concentration measurements using passive samplers can only be used to give a reasonable estimate of deposition values. The calculation of specific, more accurate and seasonal deposition velocities are beyond the scope of this study but will be part of future studies (see Chapter 6).

Zhang *et al.* (2003) developed a revised parameterisation model that improves the three-leaf resistance model (used in inferential modelling techniques for calculating dry deposition) by including non-stomatal resistance. Adon *et al.*, 2013 further adapted the parameters described in Zhang *et al.*, 2003 of land use categarories more relevant to African climate, vegetation and soil conditions. A complete description of how these deposition velocities were calculated for the different west and central African sites can be found in Adon *et al.*, 2013. It is a crude assumption made in this study to use a single deposition velocity per specie at all sites and not different values for the different seasons and/or sites. Due to this assumption, the deposition estimates follow the same trend as the annual average concentrations and will be presented and discussed on the same figures in the following sections. It is known that deposition velocities differ not only seasonally but also daily and annually. Since high resolution data that is required for the accurate calculation of deposition velocities and concentrations is not available at this stage at these remote sites, this study provide reasonable estimates based on the best available information and data. The interpretation of dry deposition values later in this chapter should, however, be treated with caution by keeping the limitations in mind.

Table 3.4: Deposition velocities (V_d) reported for dry savanna DEBITS sites in Africa[#] and values that were used in this study

Site	Country	NO$_2$ (cm s^{-1})	SO$_2$ (cm s^{-1})	HNO$_3$ (cm s^{-1})	NH$_3$ (cm s^{-1})	O$_3$ (cm s^{-1})
Agoufou[#]	Mali	0.1 – 0.2	0.1 – 0.3	0.4 – 1.2	0.1 – 0.4	0.1 – 0.2
Banizoumbou[#]	Niger	0. 1 – 0.2	0.2 – 0.3	0.4 – 1.1	0.1 – 0.4	0.1 – 0.2
Katibougou[#]	Mali	0.2 – 0.3	0.2 – 0.5	0.6 – 1.6	0.2 – 0.6	0.2 – 0.3
Values used in this study	South Africa	0.2	0.3	1.0	0.4	0.2

[#] values estimated from Figure 4 in Adon *et al.*, 2013

3 Results and discussion

3.1 Sampling period, number of samples analysed and distribution

Passive sampling was conducted at the four sites for various time periods. Sampling was initiated in 1995 at Louis Trichardt (LT), 1997 at Amersfoort (AF), 2000 at Skukuza (SK) and 2008 in the Vaal Triangle (VT). Data up to 2014 was included in the results for this chapter. A total number of 6 240 samplers were deployed at all of the sites combined and 5 617 samplers passed the quality control (Chapter 2) and outlier tests (section 2 of this chapter) (90% of all the samplers). The following table presents the number of approved results at each of the sites. AF and VT both had 93% data coverage over the respective study periods. LT and SK had 90% and 86% data coverage, respectively. The data coverage for NO$_2$, SO$_2$, NH$_3$ and O$_3$ was 93%, 90%, 94% and 94%, respectively. Data coverage for HNO$_3$, however, was only 77%. The loss of HNO$_3$ data might be due to the extremely short lifetime of HNO$_3$, which is typically only a few hours.

Table 3.5: Number (%) of approved results for each gaseous species at each of the sites

Site	Sampling period	NO$_2$	SO$_2$	NH$_3$	O$_3$	*HNO$_3$
LT	1995-2014	400 (93%)	375 (87%)	405 (94%)	406 (94%)	203 (73%)
AF	1997-2014	348 (94%)	355 (95%)	360 (97%)	353 (95%)	228 (81%)
SK	2000-2014	306 (91%)	281 (83%)	303 (90%)	306 (91%)	210 (75%)
*VT	2008-2014	158 (94%)	164 (98%)	164 (98%)	158 (94%)	*134 (80%)

Sampling of HNO$_3$ only started in 2003 at all the sites (except VT where all sampling initiated in 2008)

3.2 Inter-annual variations, deposition estimates and contextualisation

Annual average gas concentrations and annual average deposition values, calculated from the afore-mentioned gas concentrations and deposition velocities are subsequently presented. This enables the evaluation of inter-annual variation within gaseous species in an attempt to find the drivers of observed concentrations on a regional scale.

This discussion will be followed by the contextualisation of the atmospheric concentrations of the inorganic gas species determined at the sites in this study, in relation to measurements of these species in other studies conducted in South Africa, Africa as well as internationally. In the figures presented in these sections for SO$_2$, NO$_2$, NH$_3$, HNO$_3$ and O$_3$ (Figures 3.5, 3.8, 3.10, 3.12 and 3.14), values for the current study are shown on the left-hand side for each of the five gaseous species, respectively. The mean values for the sites over the entire study period are indicated using a black circle, median values are indicated with a red line, the 25th and 75th percentiles are indicated by the blue box and a 2.7% standard deviation is indicated by the whiskers (giving a 99.3% data coverage). Values from other studies conducted in South Africa, Africa and internationally are only represented by a black circle. **Exact values and references are provided in Appendix A.**

3.2.1   SO₂

Figure 3.1 provides the annual average concentrations and estimated deposition of SO_2 for each site using the deposition velocities given in Table 3.4. From Figure 3.1, a decrease in SO_2 annual average concentrations was observed for LT, AF and SK, from the inception of measurements at these sites, up to approximately 2003/2004. The measurements at VT only started in 2008 and it can therefore not be considered in this specific discussion. Since all of the previously mentioned sites (LT, AF and SK) indicated similar long-term decreasing concentration trends up to 2003/2004, even though these sites are hundreds of kilometres apart and have different local settings, it can reasonably be assumed that the downward trend in regional SO_2 concentration was real and not merely a localised artefact. One possible reason for the decrease is that global awareness and focus on air pollution/prevention also started reflecting in the South African formal economy. Many South African companies obtained quality (ISO 9000 series), environmental (ISO 14000 series) and occupational safety/health (ISO 9000 series) accreditation in this period (ISO survey, 2015). In the post-1994 democracy in South Africa, international sanctions were lifted. This implied that many local companies could start international trade. However, international trade requires international accreditation. Specifically, the ISO 14000 series environmental accreditation requires a company to apply certain minimum environmental standards that are governed by procedure, and that the company indicated continued improvement. Although de-SO_x technology is not applied by many companies in South Africa, some large metallurgical smelters that emitted high pollutant concentrations even started applying such technology as part of the minimum requirements and continued improvements required by ISO 14000 series accreditation (e.g. Westcott *et al.*, 2007). However, after 2004 up to 2008, annual average concentrations of SO_2 increased at these three sites (LT, AF and SK), possibly since the rapid growth of industrial and household activities in South Africa (Vet, *et al.*, 2014) started outweighing improvements made due to increased environmental awareness. The economic and consumption growth in South Africa is confirmed by electricity consumption, which increased significantly in the period 2002 to 2004 (e.g. Menyah & Wolde-Rufael, 2010; Statistics South Africa, 2012). However, in 2007/8, the global financial crisis occurred (considered by many to have been the worst financial crisis since the Great Depression of the 1930s) (e.g. Barrell & Davis, 2008; Bordo, 2008; Eichengreen & O'Rourke, 2009), which resulted in many of the South African commodity-based producers (e.g. platinum group metal, base metal, ferrochromium, ferromanganese, ferrovanadium and steel smelters) totally stopping production in late 2007 or in 2008. For instance, ferrochromium production in SA decreased by approximately 35% from 2007 to 2009 (ICDA, 2013), and energy consumption in the manufacturing sector dropped by approximately 34% from 2007 to 2008 (Statistics South Africa, 2012). These stoppages and/or

declines in commodity-based production are likely to have contributed significantly to the sharp decline in SO_2 concentrations post-2007/8. Many of these commodity-based smelters emit significant volumes of SO_2 (e.g. Westcott *et al.*, 2007, who indicated 2.1 to 5.8 kg SO_2 per ounce of platinum produced). Up to 2014, which correlates with the data coverage, the commodity-based marked had not yet recovered to pre-2007/8 levels.

Figure 3.1 illustrates the above-mentioned increases and decreases in SO_2 concentrations and deposition.
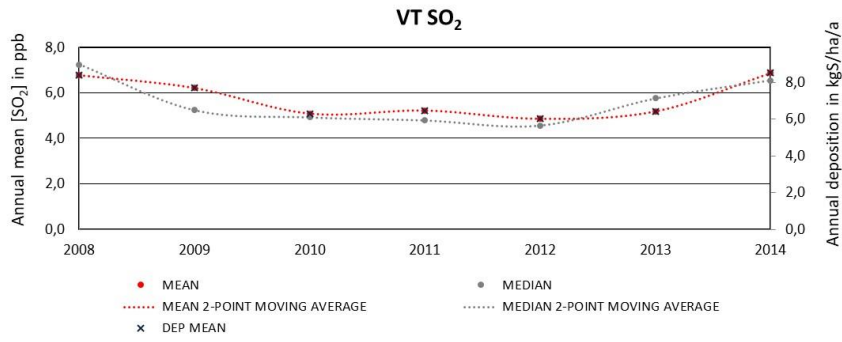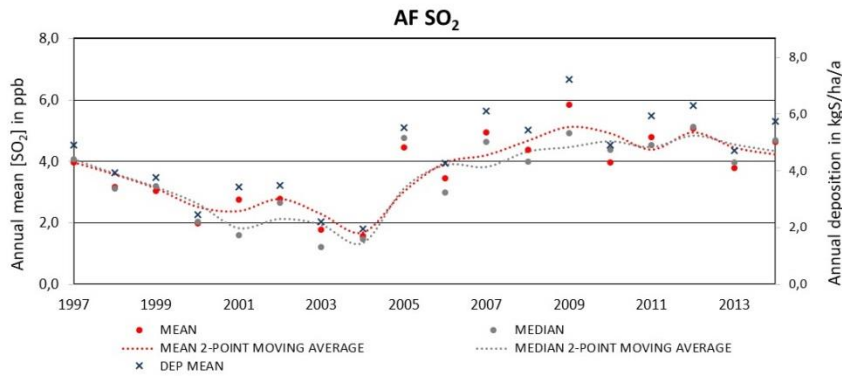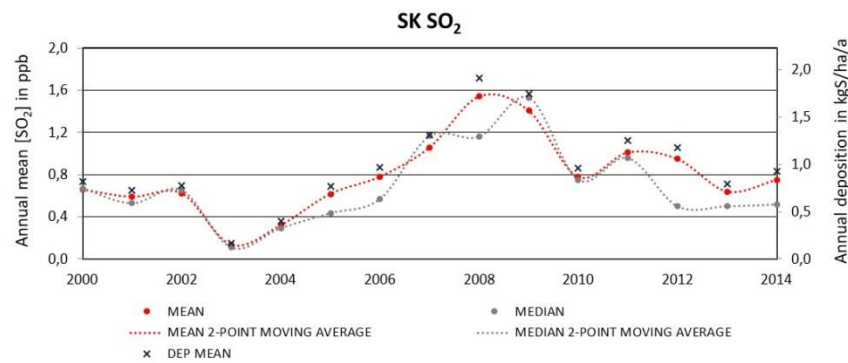
Figure 3.1: Annual average concentrations and deposition estimates of SO$_2$ (note the different time scales and concentrations) at (a) Vaal Triangle; (b) Amersfoort; (c) Skukuza and (d) Louis Trichardt

Another observation from the data is that AF, SK and LT (Figure 3.1) followed approximately the same inter-annual trend of SO_2 concentrations, while measurements at VT remained relatively constant, indicating a strong, constant influence of industry on the measurements at this site as is reflected by the relatively high values. The decrease in SO_2 concentrations measured at AF, SK and LT, respectively, indicates that the industrial influence decreases as the air masses travel further from the industrial region, as can be seen from the lower concentrations measured at SK and even lower concentrations measured at LT. In order to evaluate and illustrate the influence of air mass circulation, overlaid back trajectories were compiled for each site as an example, using 2009 and 2010 data. These two years were selected for a number of reasons, one being that the years selected should show a significant difference in concentration in order to evaluate the influence of air mass circulation. Another reason for choosing 2009 and 2010, and not e.g. 2004/2008, is that the years selected should preferably be consecutive years in order to eliminate as many big changes as possible (such as the implementation of new air quality policies, economic growth and population growth). The air mass history for each site for 2009 and 2010 was determined by calculating back trajectories as described in Chapter 2 of this thesis. In Figure 3.2, the dominant air mass movement patterns towards the sites are indicated for the combination of 2009 and 2010 data. As is evident from Figures 3.2 (a) and 3.2 (b), both the VT and AF sites have air mass back trajectory regions that are significantly influenced by the major anthropogenic activities in the industrialised areas of SA. The industrial influence decreases as the air masses travel further from the industrial region, as is indicated throughout the result section by the lower concentrations at the SK and LT sites.

Furthermore, the VT and AF sites (Figures 3.2 a and b) are affected more by the anticyclonic circulation that is characteristic of the Mpumalanga Highveld region. The Highveld region is also prone to the formation of inversion layers due to limited cloud cover and high pressure systems, high altitude and subtropical subsidence and low heat capacity of the soil, resulting in the reduction of vertical mixing (Laakso *et al.*, 2012), with the daily maximum planetary boundary layer (PBL) top height reaching 2 260m in October and 1 480m in June (Korhonen *et al.*, 2014). The meteorological conditions of the Highveld can result in the trapping of pollutant species over the country for several days (Laakso *et al.*, 2012).

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(a)

(b)

(c)

(d)
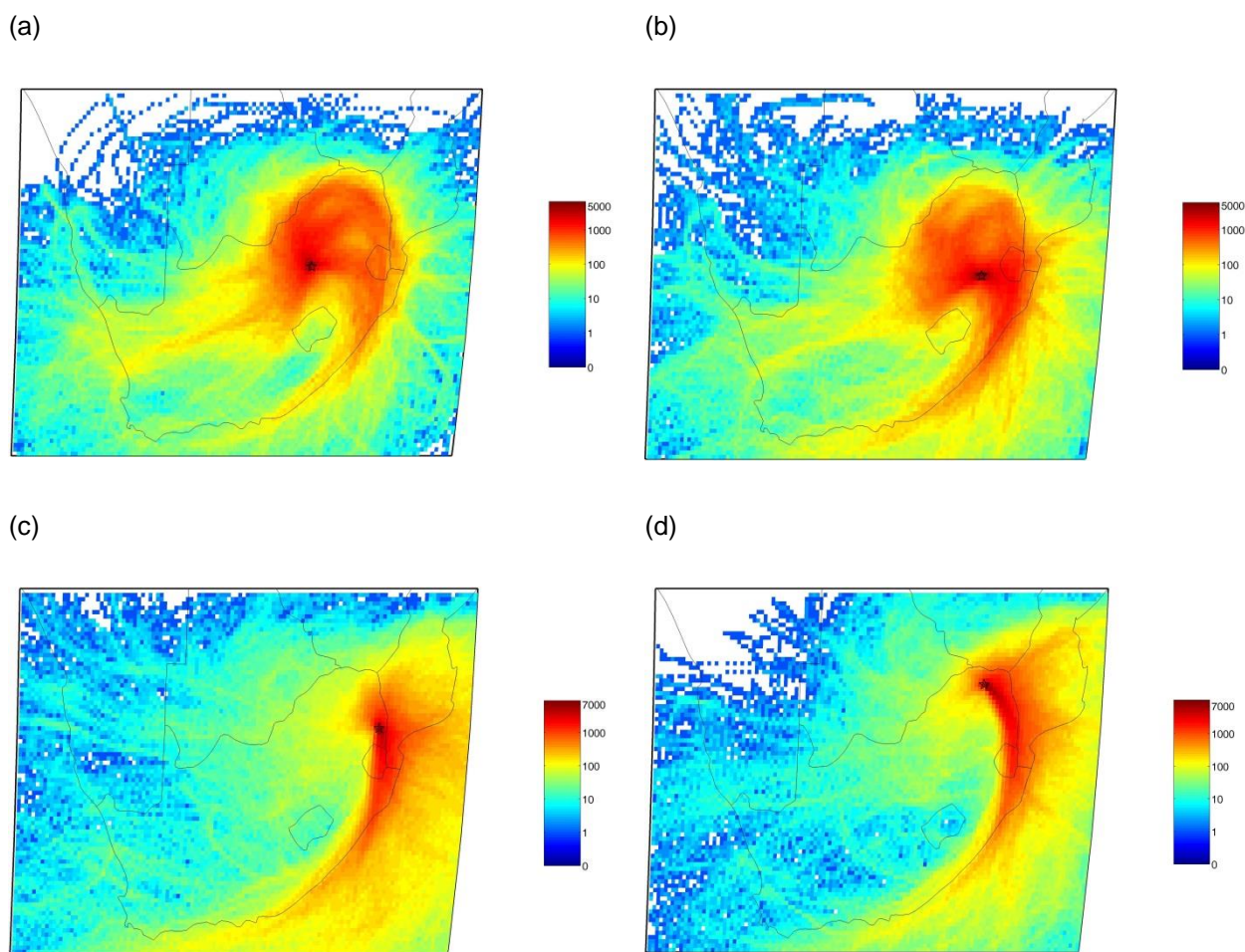
Figure 3.2: Overlay back trajectory analyses for air masses arriving at VT (a), AF (b), SK (c) and LT (d) for 2009 and 2010 combined

In a similar manner as described above, another possible reason for variations in inter-annual concentrations measured might be due to changes in the inter-annual circulation of air masses. To evaluate and illustrate this, Skukuza circulations in 2009 and 2010 *respectively* were selected. Overlaid back trajectories were compiled in the same manner as described in Chapter 2 and as presented above in Figure 3.2.

Figure 3.3 indicates that air masses travelled more over the coastal regions in 2009 (Figure 3.3 (a)), while in 2010, air masses came in a bit more off-shore and over the seaside (Figure 3.3 (b)).
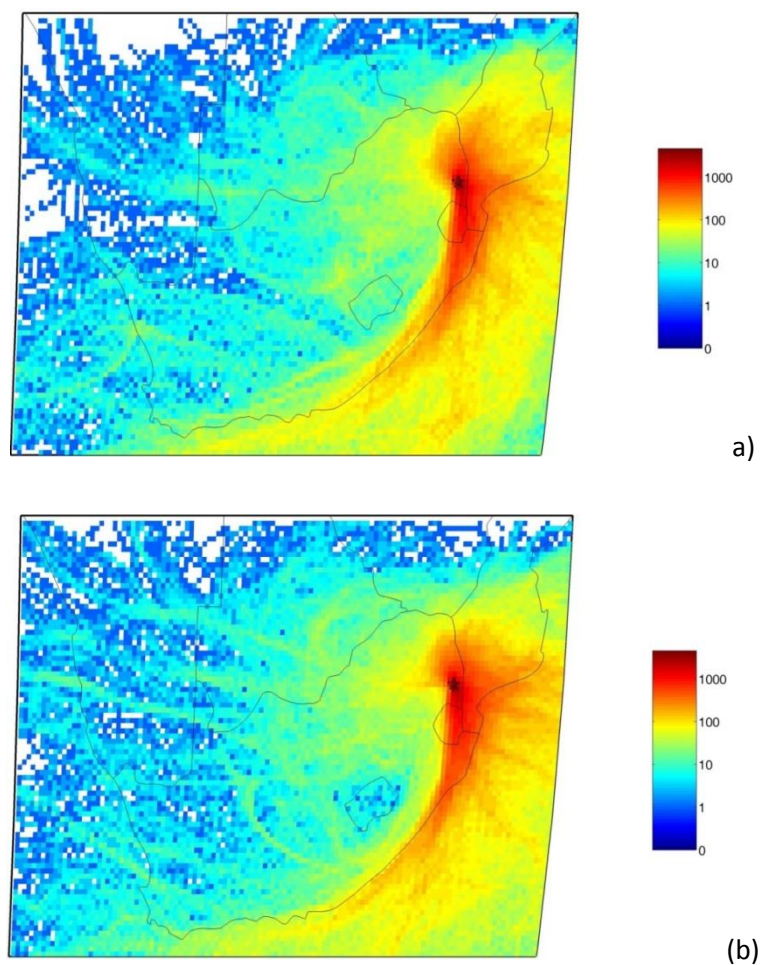
Figure 3.3: Overlay back trajectory analyses for air masses arriving at Skukuza for (a) 2009 and (b) 2010

The coastal regions are densely populated (Figure 3.4) and populated regions are linked to higher fossil fuel combustion, biomass burning (natural and for household purposes), traffic emissions and industrial activities that are significant sources of SO_2 emissions (Wallace & Hobbs, 2006; Fenger, 1999; Brimblecombe, 1996), whereas marine sources of SO_2 comprise the conversion of DMS, COS, CS_2 and H_2S to SO_2 (Wallace & Hobbs, 2006; Van Loon & Duffy, 2005). For these reasons, it can be hypothesised that this slight shift in direction from where the air masses originated in 2009 compared to 2010 (Figure 3.3) might also have contributed to the higher annual SO_2 concentrations observed at Skukuza during 2009.

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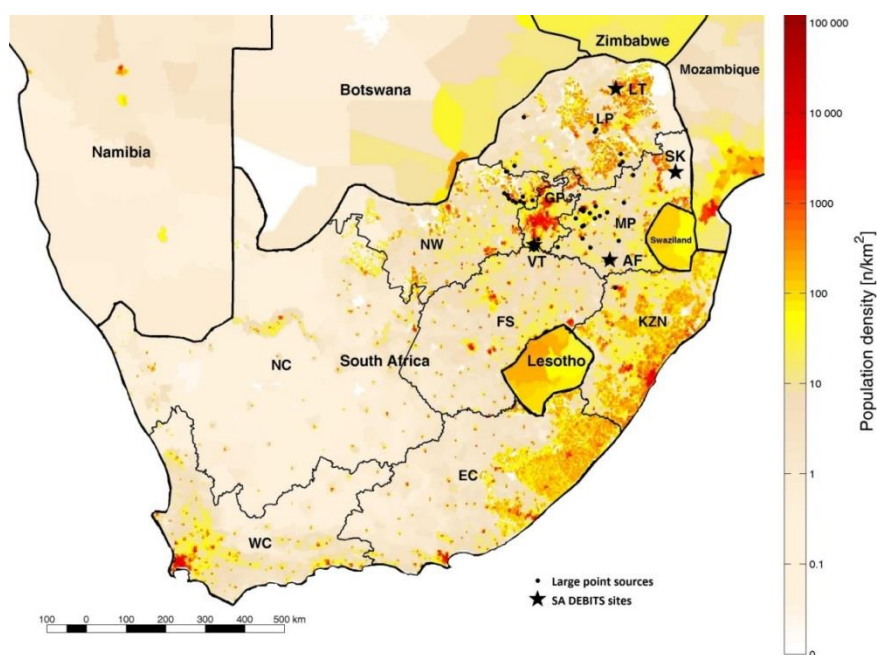
Figure 3.4: Population density of South Africa

In a recent global assessment of precipitation and deposition, South Africa was identified as an area of high S deposition, with modelled estimations in the range of 4.0 to 12.0 kg S/ha/a (Vet *et al.*, 2014). The authors further estimated that dry deposition of sulphur makes up more than 70% of total S deposition in southern Africa (Vet *et al.*, 2014). Areas with rainfall less than 40 cm a^{-1} also appear to have high dry deposition ratios, but in the range 50 to 70% (Vet *et al.*, 2014).

The highest annual average SO_2 deposition for this study was estimated at the sites impacted by industrial activities, namely AF with a value of 4.6±1.5 kg S/ha/a, and VT with a value of 7.1±1.0 kg S/ha/a. These sites are much higher when compared to SK and LT, with values of 1.0±0.4 kg S/ha/a and 0.9±0.5 kg S/ha/a, respectively. The annual average dry sulphur deposition contributed by SO_2 ranged from 6.0 to 8.5 kg S/ha/a at VT, 2.0 to 7.2 kg S/ha/a at AF, 0.7 to 1.9 kg S/ha/a at SK and from 0.4 to 1.9 kg S/ha/a at LT. All of these ranges are higher compared to observations at west and central African sites, where low measured concentrations of SO_2 are found in the absence of industrial and other anthropogenic activities (Adon *et al.,* 2010; 2013).

Figure 3.5: Annual average concentrations of SO₂ at Vaal Triangle (VT); Amersfoort (AF); Skukuza (SK) and Louis Trichardt (LT). Values of Africa as well as global values were added to the left in order to contextualise SA data. The mean is indicated by the black circles, the median by the red line, the 25th and 75th percentiles by the blue box and the whiskers indicating a ±2.7 standard deviation which gives a 99.3% data coverage (if a normal distribution is assumed). Furthermore, the maximum measured value at each site is indicated above the box and whisker plot

From Figure 3.5 (Exact values and references are provided in Appendix A)., it can be seen that the sites impacted by industrial activities, namely AF and VT, showed mean SO₂ concentrations that are much higher than other studies conducted in Africa. AF had an annual average concentration of 3.7 ppb, while 5.7 ppb was observed at the VT site (Figure 3.5). Previous reported results for SO₂ concentrations measured at AF were 2.8 ppb for the time period 1995 to 2005 (Martins *et al.*, 2007). These two sites also compared well with other South African studies at sites that are situated within highly polluted areas (Lourens *et al.*, 2011; Carmichael *et al.*, 2003). Witbank, one such site that is situated within a SA air pollution priority area, had an annual average value of 13.3 ppb, indicating that the nearby metropolitan area has a significant impact on the regional air quality (Lourens *et al.*, 2011). A few of the measurements reported at other international sites were within the same range observed at Amersfoort, such as Meixian (Southern China), which had an annual average value of 4.2 ppb (Meng *et al.*, 2010), Cochin (a regional background site in India) and Marcapomacocha (a regional background site in Peru) with annual average values of 4.8 ppb and 3.1 ppb, respectively (Carmichael *et al.*, 2003). A few international studies ranged the same as observed for the Witbank site (13.3 ppb) in another SA study (Lourens *et al.*, 2011), for instance Lin'an, a regional background

site in Eastern China had published values of 13.1 ppb (Carmichael *et al.,* 2003) and 13.9 (Meng *et al.,* 2010).

In contrast to VT and AF, the two regional background sites at SK and LT have relatively low SO_2 concentrations. This was similar to observed measurements at other west and central African sites. An annual average SO_2 concentration of 0.8 ppb was observed at SK, while 0.7 ppb was observed at Louis Trichardt (Figure 3.5). Similar concentrations at other African sites include: 0.6 ppb at Banizoumbou (Niger, dry savannah) and Katibougou (Mali, dry savanna), 1.0 ppb at Agoufou (Mali, dry savannahs), 0.5 ppb at Lamto (Cote d'Ivoire, wet savanna) and 0.8 ppb at Djougou (Benin, wet savannahs) (Adon *et al.*, 2010). Internationally, similar concentrations were reported for numerous sites in Taiwan, Japan, Malaysia, Laos, Nepal, French Guiana, Argentina, Chile and Brazil by Carmichael *et al.* (2003).

3.2.2 NO_2

Figure 3.6 illustrates the NO_2 concentrations at the sites in this study. A differentiation between sites that are being influenced by anthropogenic activities (VT and AF), and the sites that are more regionally representative and showing slight influence of transported chemical species (SK and LT) was observed, as was indicated in the previous section and Figure 3.2. The difference in concentrations between SK and LT can be ascribed to a number of reasons. For instance, the distance from the highly-industrialised Highveld priority area is greater at LT than at SK, resulting in less transported NO_2 influencing LT due to the relatively short lifetime of NO_x in the troposphere due to its reactivity (refer to section 1.4.3 of this chapter) (the same holds true for SO_2 in the previous section). Another contributing factor might be the location of the SK site. SK is situated within the Kruger National Park, a famous tourist attraction in South Africa and rated as one of the top tourism attractions in South Africa, with an estimated number of one million tourists visiting the Kruger National Park per annum (Saayman & Saayman, 2006) and therefore SK would be subjected to a much higher traffic volume and higher traffic emissions than at Louis Trichardt.
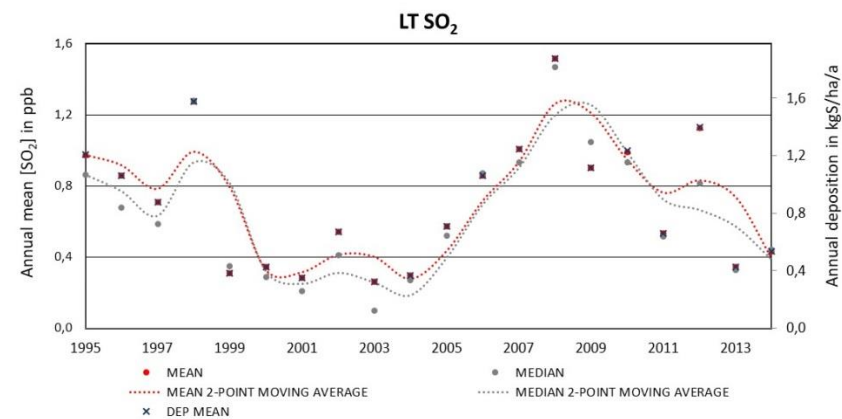
Figure 3.6: Annual average concentrations and deposition estimates of NO₂ (note the different time scales and concentrations) at (a) Vaal Triangle; (b) Amersfoort; (c) Skukuza and (d) Louis Trichardt

Another observation from the data is the substantial increase in NO_2 concentrations at all sites in 2011 and 2012 (Figure 3.6). An evaluation of the complete dataset showed similar increases for NH_3 (Figure 3.9), but not for the other gaseous species of interest in this study. Numerous possibilities were evaluated in order to interpret this increase. Possible contributions from coal combustion, power generation and the petrochemical industry were not considered due to the SO_2 (Figure 3.1) concentrations that did not indicate the same pattern as was observed for NO_2. One possible contributing factor to the observed increase in NO_2 (and subsequently NH_3 due to the oxidation of NO_2) concentrations could be a higher occurrence of veld fires. To investigate this, veld fire inventories for 2009 and 2011 were compared and were mapped (Figure 3.7). From Figure 3.7, it can be concluded that more veld fires occurred in 2011 than in 2009, and therefore it can be assumed that the higher occurrence of veld fires (not only over Botswana, but over the interior of SA as well) possibly contributed to the higher concentrations of NO_2 and NH_3 that were observed. However, this increase alone cannot explain the big differences in NO_2 concentrations (refer to Section 3.2.3 for discussion on NH_3 concentrations).

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(a)

(b)
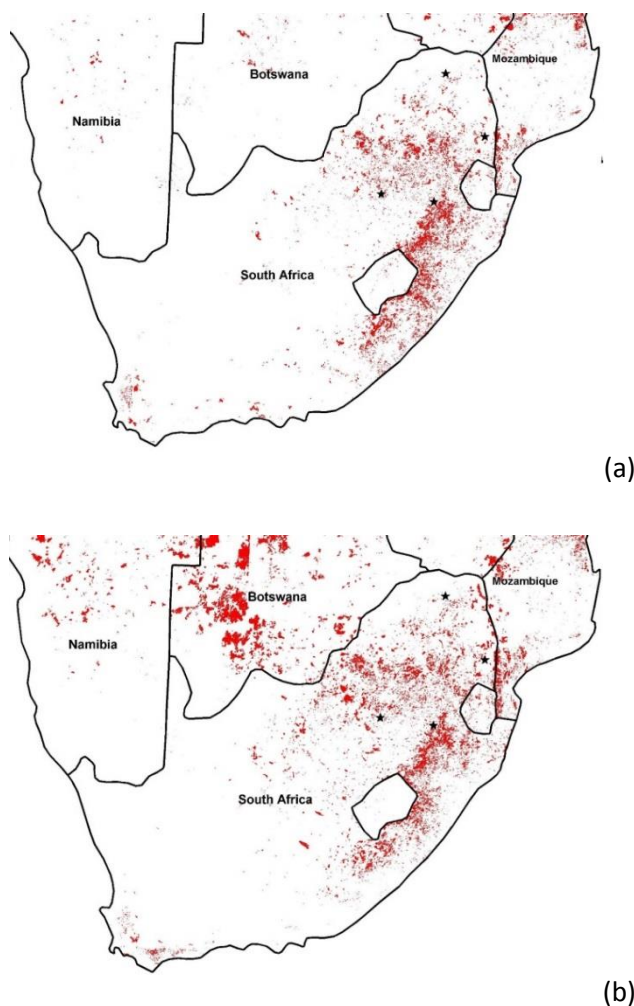
Figure 3.7: Occurrence of veld fires during (a) 2009; and (b) 2011

During this study, the highest annual average NO_2 deposition (converted to N deposited) was observed at VT (5.3±2.4 kgN/ha/a), followed by AF (1.3±0.6 kgN/ha/a). The deposition values correspond with the concentrations due to the use of a constant deposition velocity (refer to section 2 of this chapter). This is a limitation that needs to be addressed in future studies. The value at VT is higher than that estimated in the global assessment for South Africa (approximately 2-4 kgN/ha/a) (Vet *et al.,* 2014) but VT is not a remote site but a heavily impacted metropolitan site. SK and LT had much lower annual average NO_2 depositions with values of 0.4 kg N/ha/a and 0.3 kgN/ha/a, respectively. The estimated deposition values are in reasonable agreement with that calculated by Vet *et al., 2014.* Figure 3.8 shows the sites of this current study in context to a few other studies by comparing concentrations. The annual average dry deposition of NO_2 ranged from an estimated minimum of 2.8 to a maximum of 9.2 kgN/ha/a at VT (Figure 3.6(a)), from 0.4 to 2.7 kgN/ha/a at AF (Figure 3.6(b)), SK deposition estimates (Figure 3.6(c)) ranged from 0.1 to 1.1 kg N/ha/a and LT estimates (Figure 3.6(d)) ranged from 0.1 to 0.5 kg N/ha/a.

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From Figure 3.8 (Exact values and references are provided in Appendix A.), it can be seen that AF had annual average NO_2 concentrations almost three times higher than that observed at SK at 3.5 ppb. The highest concentration was observed at VT (14.6 ppb). NO_2 annual average concentrations in *other* SA studies also indicate differences between sites that are impacted more strongly by industrial activities and sites that can be regarded as background sites (Figure 3.8). The groupings with higher concentrations are all from sites that are situated within the polluted Highveld Priority area, with annual average values ranging from 6.2 ppb in Standerton to 9.2 ppb in Delmas (Lourens *et al.*, 2011). The lowest annual average NO_2 concentrations were measured at LT (0.8 ppb), followed by SK at 1.2 ppb (Figure 3.8).
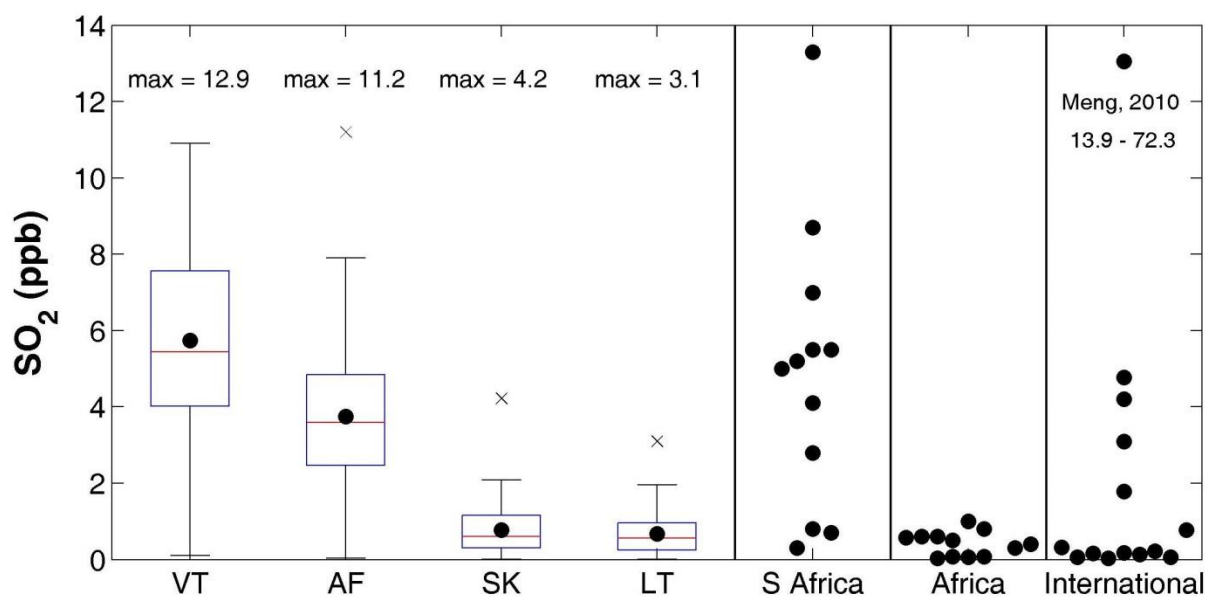

Figure 3.8: Annual average concentrations of NO_2 at Vaal Triangle (VT); Amersfoort (AF); Skukuza (SK) and Louis Trichardt (LT). Values of Africa as well as global values were added to the left in order to contextualise SA data. The mean is indicated by the black circles, the median by the red line, the 25th and 75th percentiles by the blue box and the whiskers indicating a ±2.7 standard deviation which gives a 99.3% data coverage (if a normal distribution is assumed). Furthermore, the maximum measured value at each site is indicated above the box and whisker plot

As a comparison to the rest of the continent, SK and LT agree well with values observed at west and central African sites, classified as dry savanna, wet savanna and forest and ranging between 0.9 ppb (Zoetele, Cameroon) and 2.4 ppb at Banizoumbou (Niger) (Adon *et al.*, 2010). Global measurements indicated that measurements in California (1.3-2.0 ppb) had similar concentrations as SK and LT (Bytnerowicz *et al.*, 2002), while Meng *et al.* reported significantly higher values in China, ranging

between 8.5 ppb (Kaili, South-western China) and 26.6 ppb (Houma, Northern China) (Meng *et al.*, 2010).

3.2.3 NH$_3$

Annual average concentrations of NH$_3$ (Figure 3.9) ranged from 1.2 ppb to 7.8 ppb at VT, 0.4 to 3.4 ppb at AF, 0.4 to 2.3 ppb at LT and from 0.3 ppb to 1.8 ppb at SK. The measured NH$_3$ annual average concentration at each site (Figure 3.9) followed a very similar cycle compared to NO$_2$ (Figure 3.6), strengthening the hypothesis that the substantial increase in the values in 2011 can most likely be interpreted as being due to the increase in the occurrence of veld fires in 2011 (Figure 3.7) that caused an increase in NO$_2$ concentrations and subsequently an increase in NH$_3$ concentrations. However, the observed increase in NH$_3$ concentrations at VT was four times higher in 2011 compared to 2010, while the NO$_2$ concentrations were only 1.5 times higher. This led to the assumption that the oxidation of NO$_2$ from veld fires could not be the only reason for the observed increase. The Vaal Triangle is a site that is strongly influenced by industrial activities and some of these industries have strong NH$_3$ emissions linked to their processes. Since NH$_3$ can be converted to NO$_2$, one can assume that the higher NH$_3$ concentration drives the increases in NO$_2$ observed in Figure 3.5. The two background sites (SK and LT) showed more annual fluctuations of NH$_3$ concentrations throughout the study period and not only an isolated increase, as was observed for VT and AF. The NH$_3$ concentrations at SK and LT are more probably linked to agricultural activities, animal urea and the use of biofuel as domestic fuel (Carmichael *et al.*, 2003) and not to industrial factors.
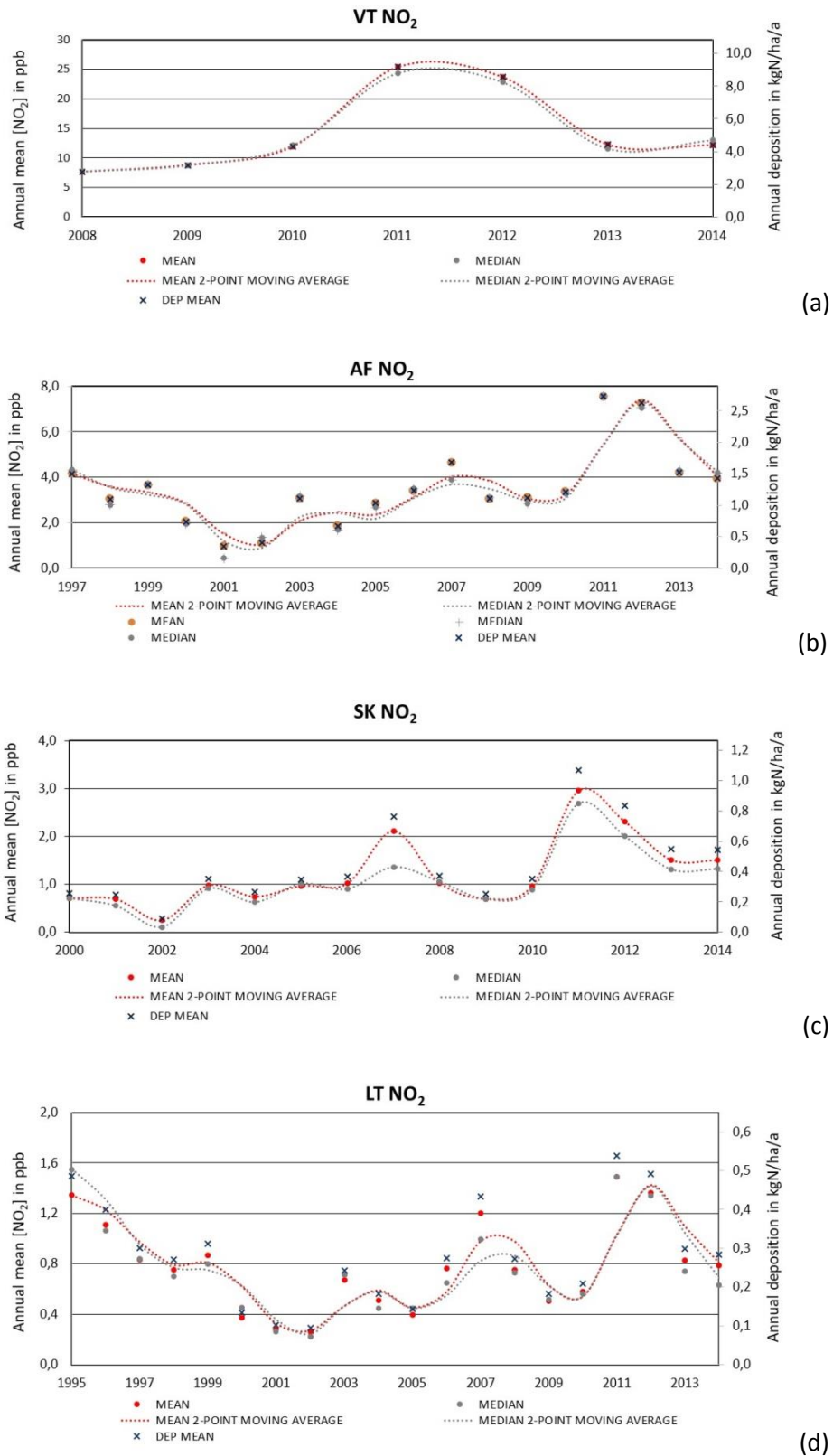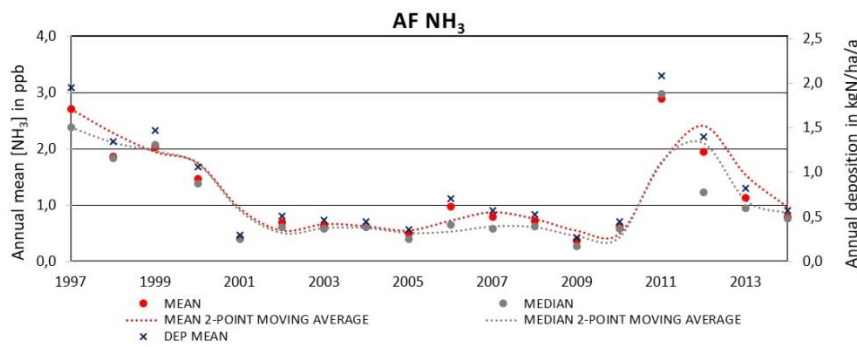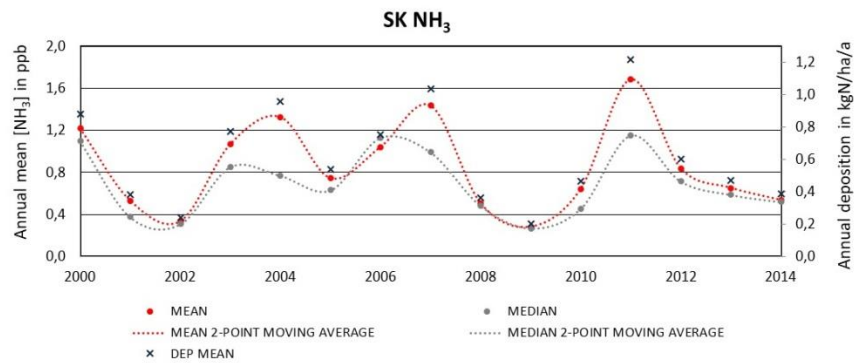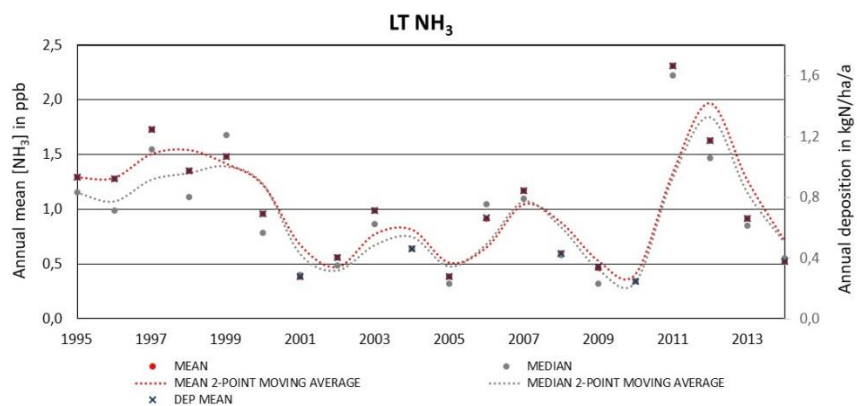
Figure 3.9: Annual average concentrations and deposition estimates of NH₃ (note the different time scales and concentrations) at (a) Vaal Triangle; (b) Amersfoort; (c) Skukuza and (d) Louis Trichardt

SO_2, NO_2 and NH_3, among others, play an important part in aerosol processes and in influencing the acidity potential of precipitation. The NH_3/SO_2 ratio of these gases offers important insight into the importance of these two gaseous species, but it is also an indication of the extent of the neutralising of NO_2 and SO_2 that might occur through NH_3 (Wallace & Hobbs, 2006). The NH_3/SO_2 ratio for this study was 0.7 at VT, 0.4 at AF, 1.1 at SK and 1.3 at LT. The influence of industrial emissions of SO_2 is again more evident at VT and AF, with ratios less than 1. Adon *et al.* (2010) reported mixing ratios above 10 at forested ecosystems (14 and 12 at Zoetele and Bomassa, respectively) and dry savannahs (11 at Banizoumbou and Katiboubou). This indicates that the industrial influence is more pronounced at all of the SA sites. Martins *et al.* (2007) reported mixing ratios of 1.5 for LT and 2.7 at Cape Point, correlating well with the values observed in this study.

The observed long-term differences in NH_3 average annual deposition (Figure 3.9) between the sites showed that the VT site had the highest annual average NH_3 deposition value (2.5 kg N/ha/a), followed by AF with 0.9 kg N/ha/a, LT with 0.7 kg N/ha/a and SK with 0.6 kg N/ha/a, respectively. The annual average NH_3 deposition values ranged from 0.8 to 5.6 kg N/ha/a at VT, 0.4 to 2.1 kg N/ha/a at AF, 0.3 to 1.7 kg N/ha/a at LT and from 0.2 to 1.2 kg N/ha/a at SK. In Vet *et al.* (2014), the global total emissions of NH_3-N were estimated at 58.5 ± 9.5 TgN, with Africa believed to contribute approximately 12.5% of this total. Total nitrogen deposition at dry Sahelian savanna ecosystems was estimated at approximately 7.5 kg N/ha/a and roughly 70% of this total is attributed to the reduced form of nitrogen (i.e. NH_3 or NH_4^+) (Delon *et al.*, 2010).

Adon *et al*. (2013) found that annual dry deposition ranged from 4.0 to 5.3 kg N/ha/a in dry savannahs, from 3.2 to 4.6 kg N/ha/a in wet savannahs and from 11.2 to 11.7 kg N/ha/a in forests if bidirectional exchange was not taken into account (Adon *et al*., 2013). These values are slightly higher than the values reported in this study.

Figure 3.10 (Exact values and references are provided in Appendix A). indicates how the sites used in this study relate to other studies in SA, Africa and internationally. In contrast to SO_2 and NO_2 contextualisation (Figures 3.5 and 3.8, respectively), NH_3 does not show the same clear distinction between the industrial and regional sites. VT did, however, still have the highest measured annual average NH_3 concentration of 3.5 ppb, with a high inter-annual variability of 84% (Figure 3.10), most likely due to the substantial increase observed in 2011/12 (Figure 3.9), as was described above. In contrast, the other three sites had more comparable annual average concentrations of 1.2 ppb at AF, 1.0 ppb at LT and 0.9 ppb at SK, all with high inter-annual variability of 67%, 53% and 49%, respectively. The inter-annual variability is much higher than observed for other African sites (ranging from 10% to a maximum of 35%) (Adon *et al.,* 2010). The biggest difference between SA

sites and other African sites is the added influence of anthropogenic sources and an urbanised way of living. The fluctuations in annual concentrations that cause the high inter-annual variations might be linked to the substantial increase observed in 2011/12 that was described above. Another contributing factor might be the differences in urban living arrangements between SA sites and other African sites. Usually, the use of biomass burning and fossil fuel combustion is infrequent and as needed in SA, while the use of biomass burning and fossil fuel combustion in households at other African sites occurs on a more fixed daily basis, and therefore the differences in inter-annual variability.

Figure 3.10: Annual average concentrations of NH$_3$ at Vaal Triangle (VT); Amersfoort (AF); Skukuza (SK) and Louis Trichardt (LT). Values of Africa as well as global values were added to the left in order to contextualise SA data. The mean is indicated by the black circles, the median by the red line, the 25th and 75th percentiles by the blue box and the whiskers indicating a ±2.7 standard deviation which gives a 99.3% data coverage (if a normal distribution is assumed). Furthermore, the maximum measured value at each site is indicated above the box and whisker plot

Annual average concentrations ranged from 1.2 ppb to 7.7 ppb at VT, 0.4 to 2.9 ppb at AF, 0.4 to 2.3 ppb at LT and from 0.3 ppb to 1.7 ppb at SK (Figure 3.10). The annual average concentrations are much lower in SA compared to other IDAF sites (minimum of 3.9 ppb at Djougou, up to a maximum of 7.4 ppb at Agoufou) (Adon *et al.*, 2010). The AF, SK and LT annual average values ranged lower when compared to other international values. Some international values ranged below 1 ppb (such as Oki (Japan) and Tanah Rata and Lawa Mandau (Malaysia)) and were not included in Figure 3.10

(Carmichael *et al.*, 2003), while some measurements, such as Houma (Northern China), measured as high as 13.9 (Meng *et al.*, 2010) and even greater than 40 ppb (Agra, India) (Carmichael *et al.*, 2003).

3.2.4   HNO$_3$

The long-term results for HNO$_3$ (Figure 3.11) do not follow similar trends when compared to trends observed for NO$_2$ (Figure 3.6), even though there exists a chemical linkage between the two species. Unlike NO$_2$ and SO$_2$, there were no substantial differences in annual average concentrations between the four sites. This is an unexpected result, as NO$_2$ is the only source of atmospheric HNO$_3$, and therefore one would expect that the two industrially impacted sites with higher NO$_2$ concentrations would also yield higher HNO$_3$ concentrations. A possible reason for this result could be linked to the short atmospheric lifetime of HNO$_3$ as described in Section 1.4.5 of this chapter.

The observed long-term trend in HNO$_3$ average annual deposition at VT was the highest with a deposition value of 1.9 kg N/ha/a, followed by AF with 1.7 kg N/ha/a, LT with 1.1 kg N/ha/a and SK with 1.1 kg N/ha/a. The annual average HNO$_3$ deposition values (calculated as N contributed) ranged from 1.1 to 2.7 kg N/ha/a at VT, 0.5 to 2.7 kg N/ha/a at AF, 0.3 to 2.5 kg N/ha/a at SK and from 0.2 to 1.9 kg N/ha/a at LT.

VT had an annual average HNO$_3$ concentration (Figure 3.12) of 1.0 ppb, followed by AF (0.9 ppb), LT (0.6 ppb) and SK (0.5 ppb). The HNO$_3$ concentrations compared well with data from other studies at sites in South Africa, reporting values of 0.9 ppb for Amersfoort, 0.5 ppb for Cape Point and 0.2 ppb for Louis Trichardt. The two sites at SK and LT showed values comparable to annual average concentrations of dry savannah sites (0.5 ppb) that were calculated over a 10-year period at Banizoumbou (Niger) and Agoufou (Mali) (Adon *et al*., 2010). However, the sites at VT and AF showed values higher than any other values observed on the rest of the continent. Since the only known source of HNO$_3$ in the lower troposphere is the removal of NO$_x$, combined with the short atmospheric lifetimes of less than one day (refer to Section 1.4.5 of this Chapter), the high level of NO$_2$ due to anthropogenic activities might be attributed to the higher values observed at VT and AF. The lower concentrations observed for HNO$_3$ when compared to the other gaseous species might also be linked to the short atmospheric lifetime of HNO$_3$.

Chapter 3
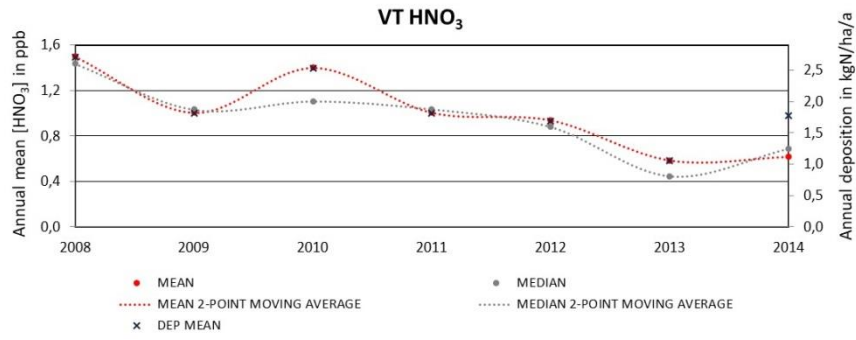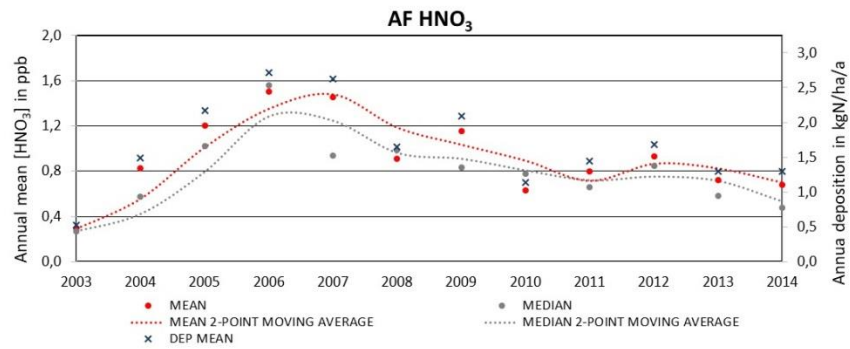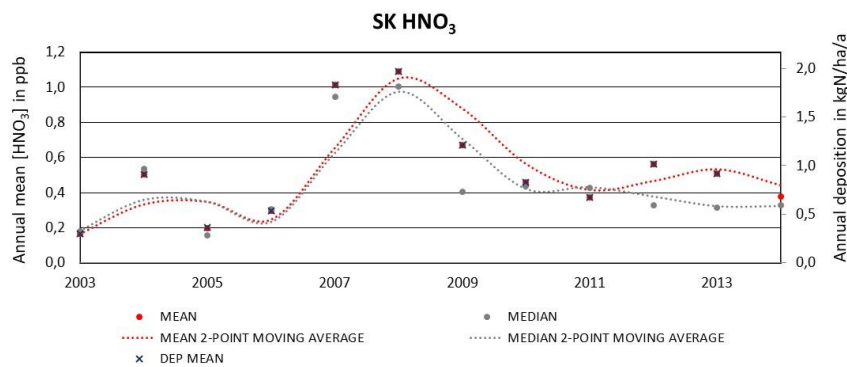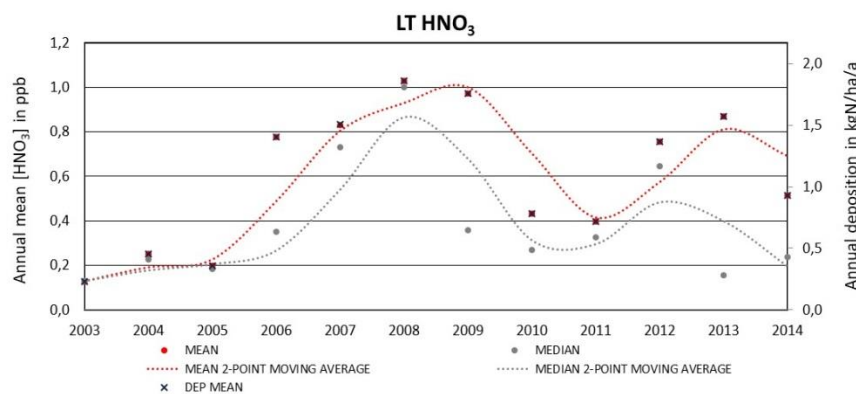
Figure 3.11: Annual average concentrations and deposition estimates of HNO₃ at (a) Vaal Triangle; (b) Amersfoort; (c) Skukuza and (d) Louis Trichardt
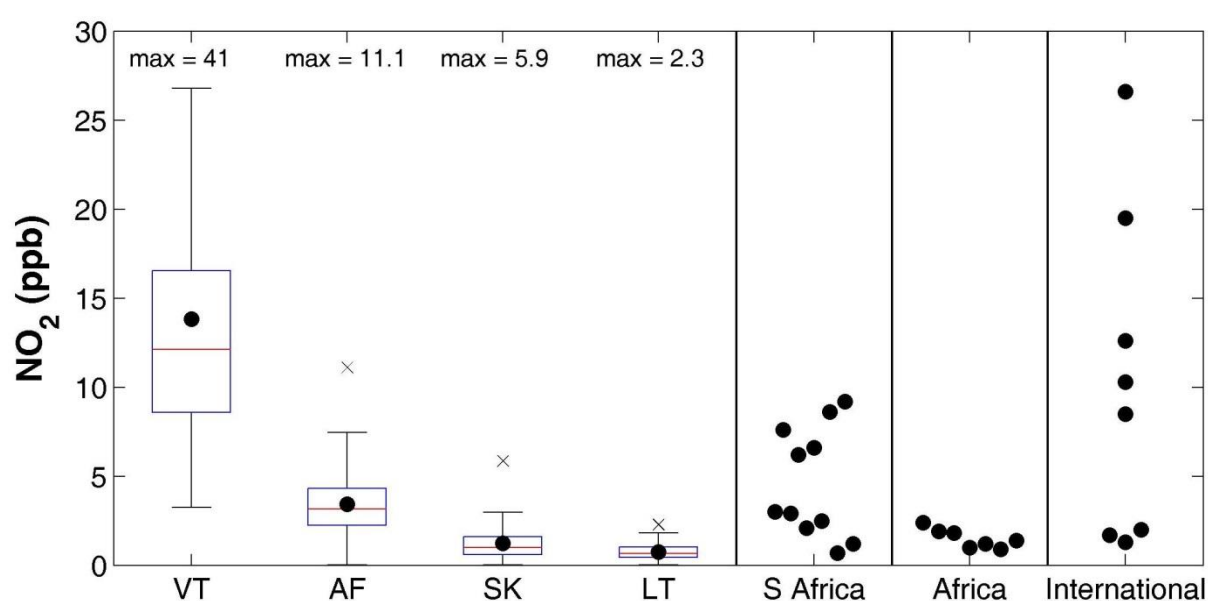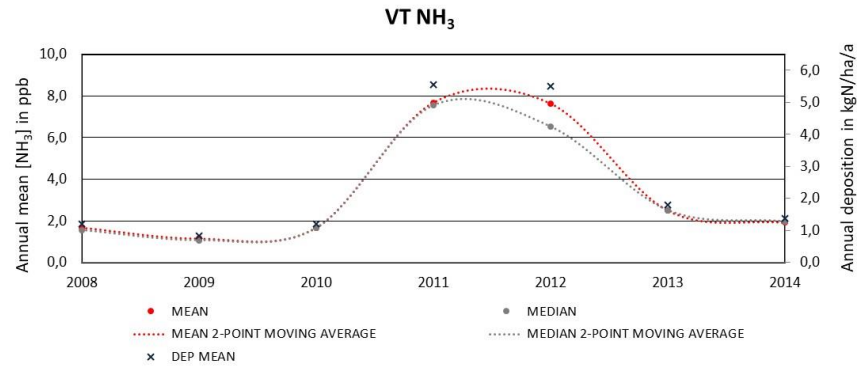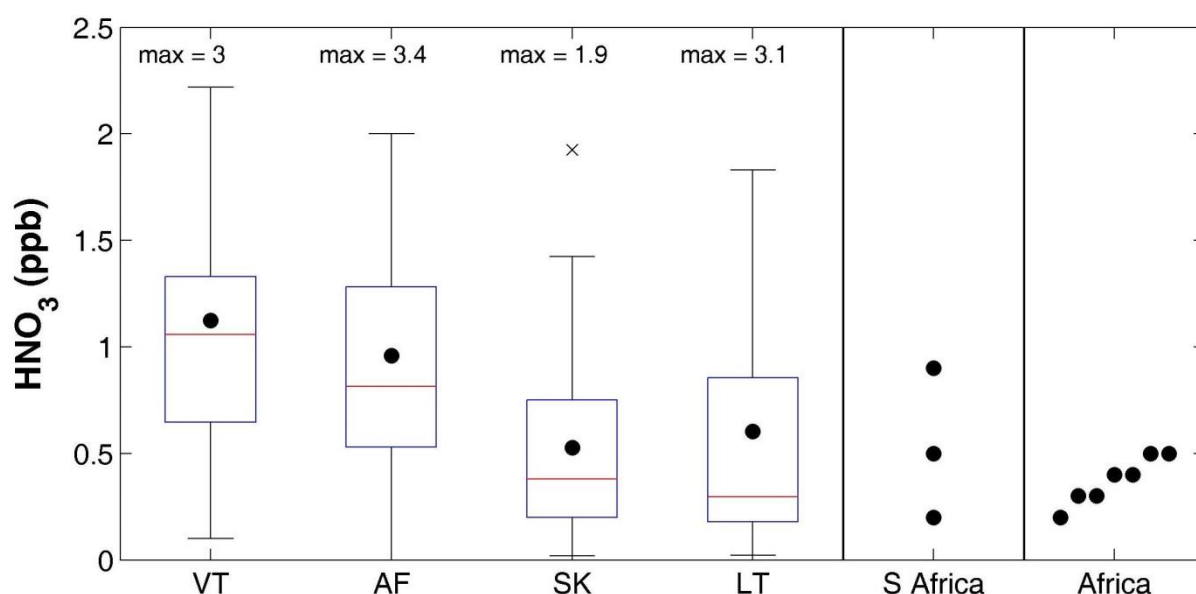
Figure 3.12: Annual average concentrations of HNO₃ at Vaal Triangle(VT); Amersfoort (AF); Skukuza (SK) and Louis Trichardt (LT). Values of Africa as well as global values were added to the left in order to contextualise SA data. The mean is indicated by the black circles, the median by the red line, the 25th and 75th percentiles by the blue box and the whiskers indicating a ±2.7 standard deviation which gives a 99.3% data coverage (if a normal distribution is assumed). Furthermore, the maximum measured value at each site is indicated above the box and whisker plot

3.2.5   O₃

The inter-annual concentrations of O_3 (Figure 3.13) followed a similar decrease up to 2001 as was observed for SO_2 (Figure 3.1) and NO_2 (Figure 3.6), strengthening the discussion in section 3.2.1 that the reason for the decrease is due to global awareness, a focus on air pollution/prevention and obtaining ISO accreditation. O_3 in the lower troposphere forms through the photochemical reactions of NO_x, volatile organic compounds (VOCs), carbon monoxide (CO) and methane (CH_4) (Seinfeld & Pandis, 2006). South Africa lies within the sub-tropical and temperate latitudes with high levels of sunshine and an abundant supply of O_3 precursor gases from the industrialised Highveld, creating an ideal atmosphere for the formation of O_3 (Zunckel *et al.*, 2004).

The annual concentrations were highest at LT and lowest at VT, similar to what was reported by (Lourens *et al.*, 2011) when comparing more rural sites to urban sites in the Mpumalanga Highveld. This is the inverse of what was observed for the NO_2 concentrations, which were highest at VT and

lowest at LT and may be ascribed to ozone titration by NO_x (Brunke & Scheel, 1998). However, numerous other factors and reactions influence the levels of O_3 measured, and therefore one must be careful not to assume that an increase in the levels of NO_2 will necessarily cause a subsequent increase in the levels of O_3. One such factor, for instance, is the distance from the precursor gas source area. When comparing VT and AF, which are both influenced by anthropogenic activities and that have an abundant supply of precursor gases available, AF had higher concentrations of O_3 compared to VT. This can be because O_3 had no time to form at VT, but was most likely consumed by other pollutant species. However, it is a well-known fact that O_3 concentrations are higher in aged pollution plumes (e.g Zunckel *et al.*, 2004). This was observed with the distance travelled and the anticyclonic circulation (Chapter 2, Figures 2.1 and 2.2; Chapter 3, Figure 3.2(a) & (b)), where the measured concentration of O_3 was higher at AF, which is downwind from the VT. Similar observations were made by Zunckel *et al.* (2004), where O_3 concentrations were higher at AF, which is located downwind from Bosjesspruit as a precursor source area. Another factor that might influence the O_3 concentrations is the height above mean sea level (amsl). During the SAFARI-92 campaign, Thompson *et al.* (1996) and Diab *et al.* (1996) reported that ozone concentrations increase with height amsl. When comparing the two background sites, for instance, SK is located at approximately 267m amsl, whilst LT is located at 1 300m amsl (Chapter 2, Figure 2.5 and section 2.2), which could explain the difference in concentrations measured at these two sites.

Annual average deposition was the highest at LT, with an average of 37 kg/ha/a and ranging from a minimum of 22 to a maximum of 69 kg/ha/a. This was followed by AF (32 kg/ha/a) ranging from 19 to 50 kg/ha/a. SK had an annual average deposition of 26 kg/ha/a, ranging between 19 and 32 kg/ha/a. VT had an annual average deposition of 20 kg/ha/a (ranging from 11 to 27 kg/ha/a), much lower than the value observed at LT, probably due to nitrogen titration at this site. The high values can most likely be attributed to abundant ozone precursor species present in the troposphere, as well as the long, sunny days experienced in South Africa (Laakso *et al.*, 2012), as was described above.
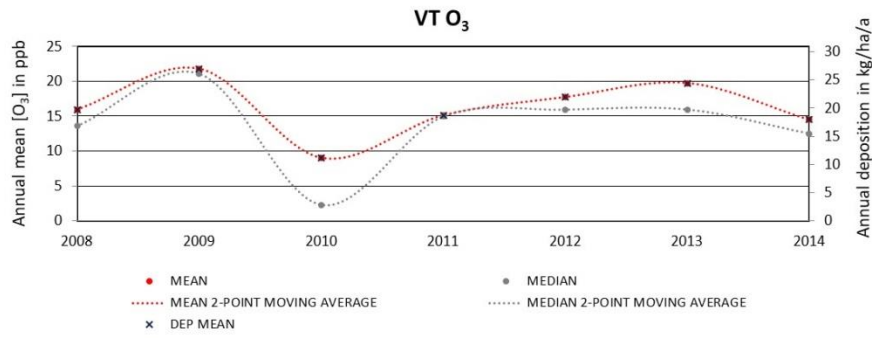
(a)
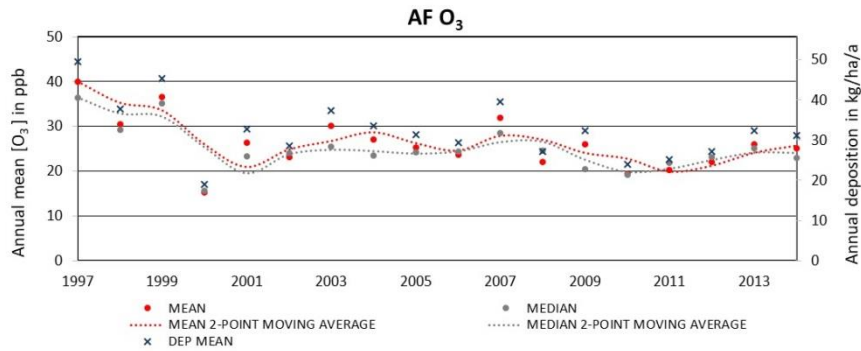
(b)
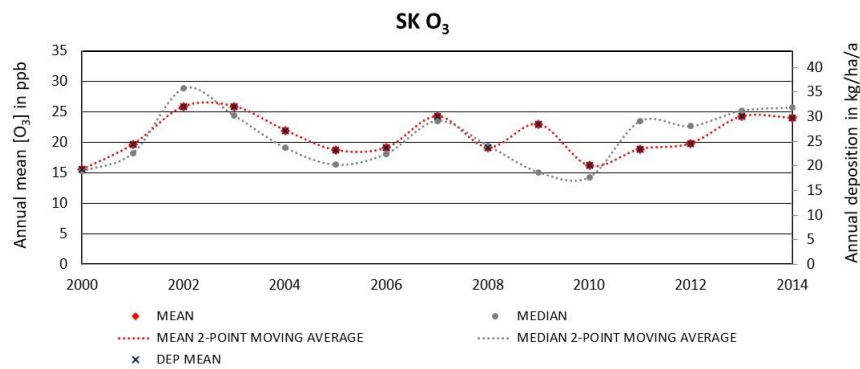
(c)
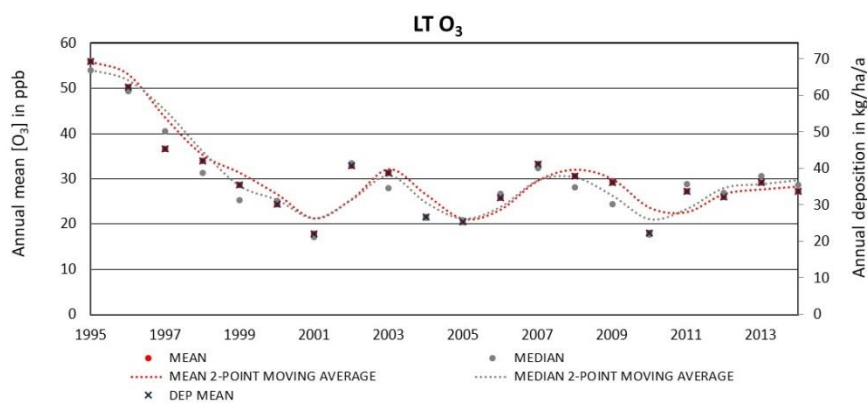
(d)

Figure 3.13: Annual average concentrations and deposition estimates of O₃ at (a) Vaal Triangle; (b) Amersfoort; (c) Skukuza and (d) Louis Trichardt

The annual average O₃ concentrations, within the context of other studies (Figure 3.14), at LT ranged from 17.9 ppb to 55.9 ppb, with a mean of 30.0 ppb. AF had annual average concentrations ranging from 15.3 to 40.0 ppb, with a mean of 26.2 ppb. SK had similar values compared to AF, with annual average concentrations in the range of 15.6 to 25.9 ppb and a mean annual average of 21.1 ppb. VT had the lowest annual average concentration of all sites, ranging between 9.1 and 21.8 ppb and with a mean annual average of 16.3 ppb. The higher levels of ozone at LT can most likely be attributed to numerous sub-continental influencing factors such as biomass burning (from SA, Zimbabwe as well as Zambia) and industrial pollutant species from the Highveld of SA that had been circulated to LT (Adon *et al.*, 2010).
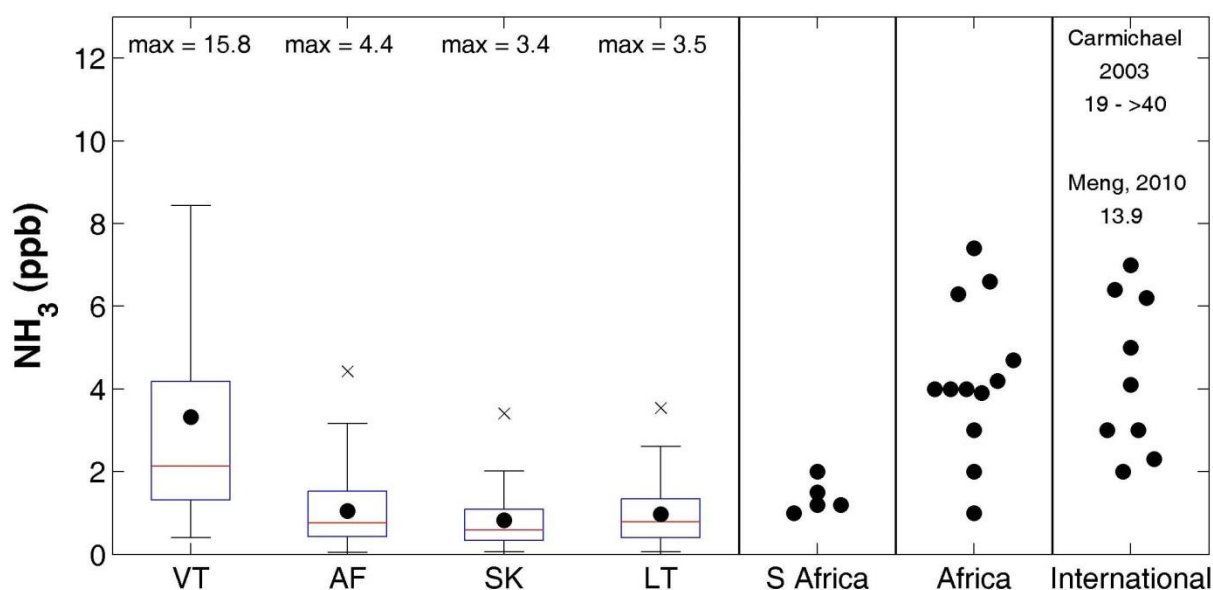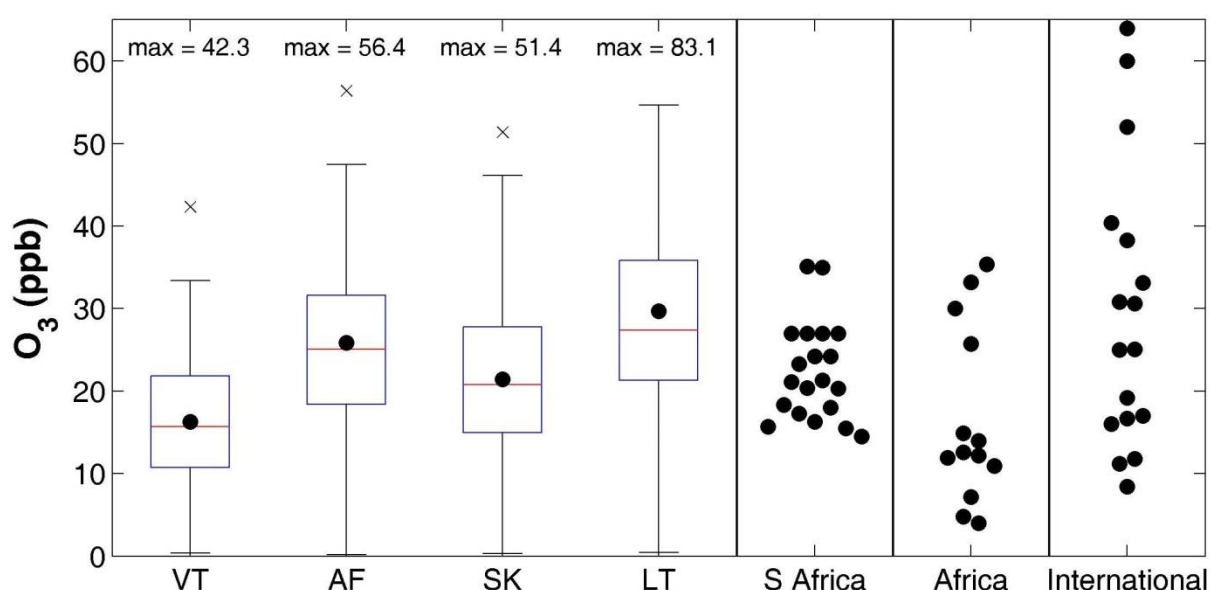

Figure 3.14: Annual average concentrations of O₃ at Vaal Triangle (VT); Amersfoort (AF); Skukuza (SK) and Louis Trichardt (LT). Values of Africa as well as global values were added to the left in order to contextualise SA data. The mean is indicated by the black circles, the median by the red line, the 25th and 75th percentiles by the blue box and the whiskers indicating a ±2.7 standard deviation which gives a 99.3% data coverage (if a normal distribution is assumed). Furthermore, the maximum measured value at each site is mentioned above the box and whisker plot

When comparing the current study to other SA studies (Lourens *et al.*, 2011; Josipovic 2009; Carmichael *et al.*, 2003; Adon *et al.*, 2010), African studies (Carmichael *et al.*, 2003; Adon *et al.*, 2010) and international studies (Carmichael *et al.*, 2003; Bytnerowicz *et al.*, 2002) (Figure 3.14), it can be seen that O₃ concentrations in South Africa range the same, irrespective of whether the measurement was made at background sites, agricultural sites, small rural sites or even industrial sites, indicating that problems that may occur due to ground-level ozone deposition are a regional

phenomenon and not site-specific. When looking at other studies, two groupings were observed, with measurements ranging from as low as 4.0 ppb in Bomassa, Congo (Adon *et al.*, 2010) and 8.4 ppb in Petit Saut (French Guiana, South America) (Carmichael *et al.*, 2003) up to 35.4 ppb in Camkoru, Turkey (Carmichael *et al.*, 2003) and even as high as 64.0 in Ash Mountain, California (Bytnerowicz *et al.*, 2002).

3.3 Seasonal variations

As discussed in Chapter 2, the meteorology of South Africa is influenced by high-pressure anti-cyclonic circulation, as well as lower PBL and formation of inversion layers that trap pollutant species, which is especially more pronounced during winter. These meteorological conditions concentrate atmospheric pollutants, which causes an increase in observed concentrations of pollutant species during the dry, winter season (May to September) (Korhonen *et al.*, 2014; Laakso *et al.*, 2012).

In Figure 3.15, the annual average rain gauge reading (Figure 3.15(a)) and average monthly temperatures (Figure 3.15(b)) from 2009 to 2013 are presented, which clearly indicate the onset of the dry winter season, which is associated with minimum rainfall. It follows from the discussion in Chapter 2 (sections 1.2, 1.3 and 2.2; Figures 2.3-2.6) that the study site at SK (situated within the Lowveld), with the lowest altitude (height above mean sea level), experiences the highest average temperatures compared to the other sites.

(a)

(b)
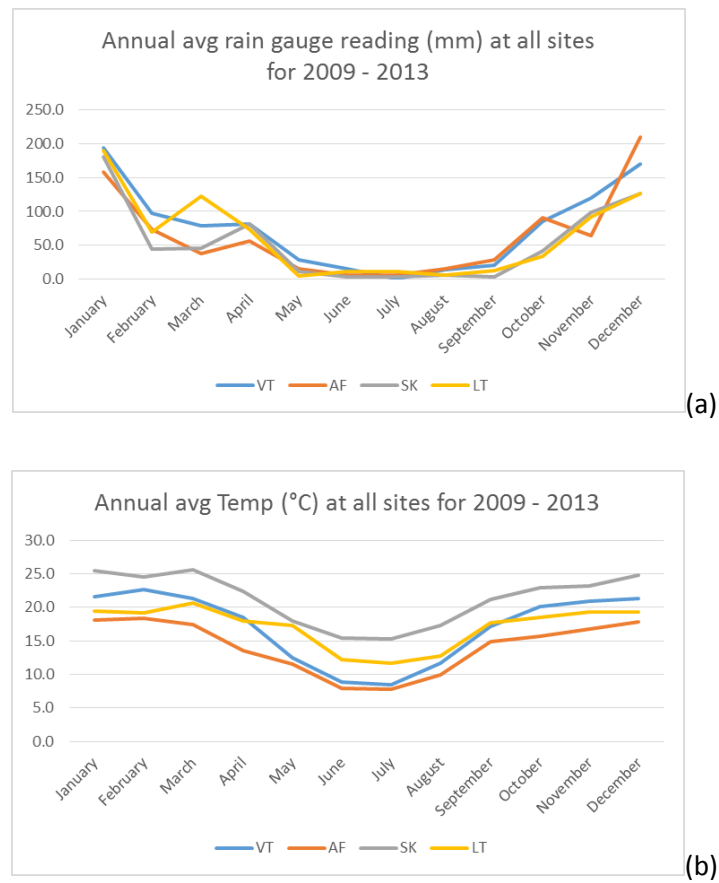
Figure 3.15: Annual average rain gauge reading (a) and annual average temperature (b) at all sites for 2009-2013

3.3.1 Seasonal variations of SO$_2$

In Figure 3.16, the seasonal patterns for SO$_2$ at all of the sites in this study are presented. It is evident from the description above that the climatology of South Africa leads to an increase in SO$_2$ concentrations. This observation is more pronounced at the two regional background sites, SK and LT (Figure 3.16(c) and (d)). Electricity and coal (both emitting SO$_2$) are used by the residential sector for normal household duties (e.g. water heating, cooking, lighting and refrigeration), but usage increases during the colder winter months, with longer nights, for space heating and extra lighting. Electricity and coal consumption accounts for approximately 50% of the energy consumption in South Africa, and 25% of all energy generated (in all forms) is consumed by the residential sector (Donev *et al.*, 2012).

The seasonal trend is not as evident at the VT site (Figure 3.16(a)) and the AF site (Figure 3.16 (b)), which are the sites that are dominated by nearby industrial emissions and therefore less likely to be influenced by rural household activities (Kleynhans, 2008; Liebenberg-Enslin *et al.*, 2007). The distribution of energy consumption in South Africa per sector indicated that 37% is used by industry (Donev *et al.*, 2012). The percentage energy use (and therefore emissions of SO$_2$) resulting from industry could account for the less pronounced increase during the winter months at the VT (Figure 3.16(a)) and AF (Figure 3.16(b)) sites, since the industrial operations at these two sites are continuous throughout the year and dominate over the household consumption of energy.

Figure 3.16: Monthly average concentrations of SO₂ for the total period at (a) Vaal Triangle; (b) Amersfoort; (c) Skukuza and (d) Louis Trichardt. The error bars indicate the standard deviation per month from all measurements over the entire study period.

3.3.2 Seasonal variations of NO_2

The average monthly concentrations of NO_2 in Figure 3.17 showed a clear seasonal increase with a maximum in early spring (end of August, start of September) at SK and LT, and to a lesser extent at AF (Figure 3.17 (b)), with the exception of VT (Figure 3.17(a)). The increase can most likely be attributed to an increase in bio-geogenic activity in the form of soil denitrification, as it marks the start of the growing season and consequently is linked to the start of the rainy season and increased soil moisture, as was indicated in Figure 3.17(c) and (d). Soil denitrification is a significant source of NO_2 (Seinfeld & Pandis, 1998; Wallace & Hobbs, 2006; Van Loon & Duffy, 2005). Denitrifying bacteria survive under anaerobic conditions by using NO_x as electron acceptors in place of oxygen and so produce reduced forms of nitrogen. Denitrification is dependent on the availability of organic matter, limited oxygen availability, availability of nitrogen oxides, and soil water (Hall & Matson, 1996). The reason why this seasonal increase is less pronounced at AF might be due to the industrial influence at this site, even though there is also a great agricultural influence at this site.

The VT site showed a different seasonal pattern, with a definite increase in mid-winter (Figure 3.17(a)). Since this site is dominated by industrial activities, the possible reason for the seasonal trend could be linked to the climatology of South Africa (as was described at the beginning of this section and in detail in Chapter 2) and trapping of pollutants during the winter months.

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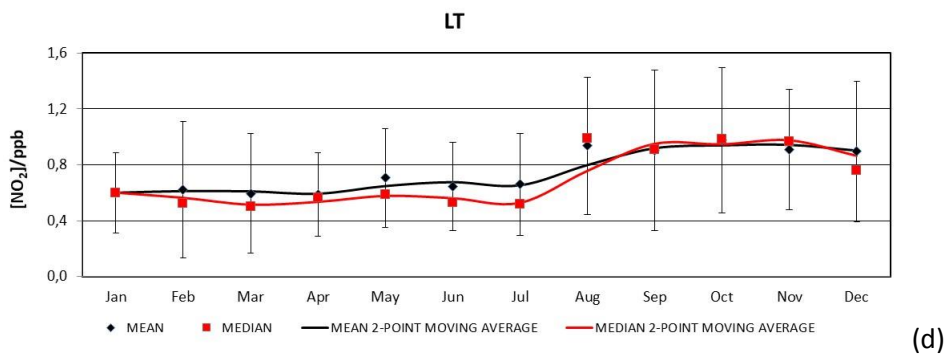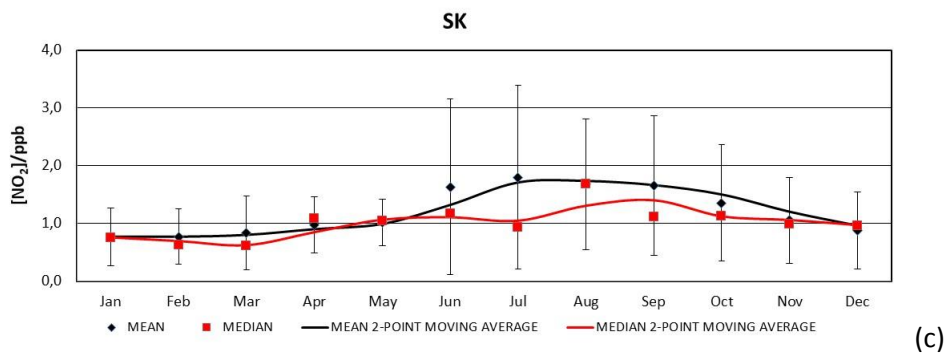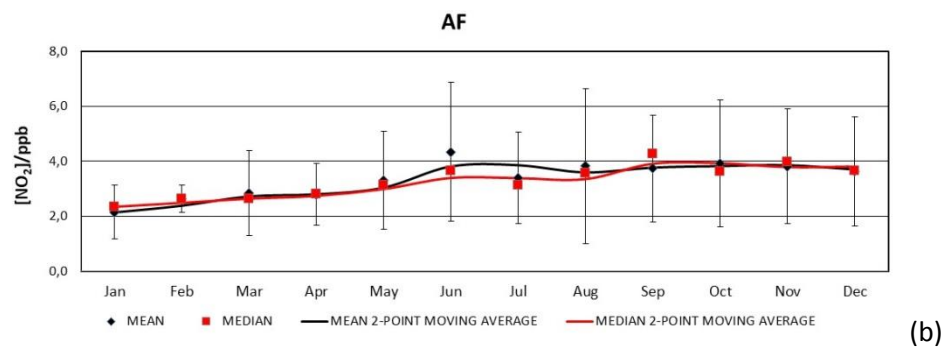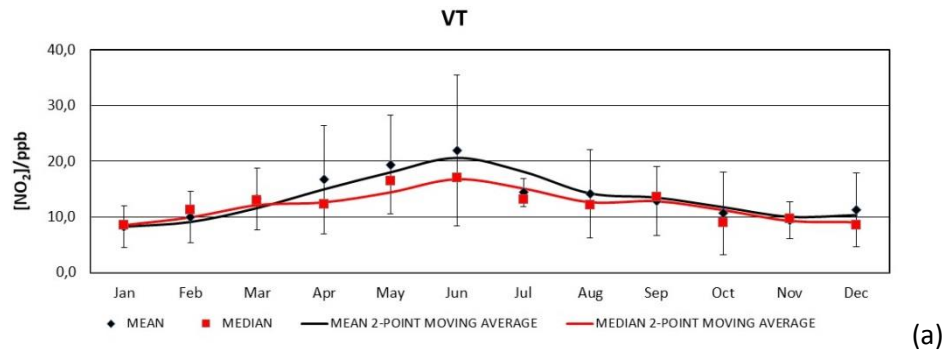
Figure 3.17: Monthly average concentrations of NO$_2$ for the total period at (a) Vaal Triangle; (b) Amersfoort; (c) Skukuza and (d) Louis Trichardt. The error bars indicate the standard deviation per month from all measurements over the entire study period.

3.3.3 Seasonal variations of NH$_3$

NH$_3$ monthly average concentrations at the SA DEBITS sites are indicated in Figure 3.18. Two different seasonal cycles are observed. The first is an increase in monthly NH$_3$ concentrations during the winter at the two sites that are influenced by industrial activities, namely VT (Figure 3.18 (a)) and AF (Figure 18 (b)). This can be linked to the climatology of South Africa, as was described earlier in this section, and the subsequent trapping of pollutant species during the cold winter months.

The second pattern shows a slight increase in observed concentrations around August and October at all the sites (Figure 3.18), coinciding with a change in seasons from dry winter to spring and the rainy season. The observed increase could be related to numerous factors. One such factor might be due to increased microbial activity, as soil moisture increases (Delon *et al., 2012*). Other factors, considered to be the major emission sources of NH$_3$ in Africa (Vet *et al.,* 2014), include bacterial decomposition of urea in animal excreta, emissions from natural and fertilised soils (Schlesinger & Hartley, 1992), savanna fires, and domestic fuel wood burning (Delmas *et al.,* 1991; Brocard *et al*., 1996). The land area in SA that is used for agricultural purposes is approximately 82%, of which less than 10% is irrigated (FAO, 2005). The study area is located within the grain agricultural region of South Africa, which produced an estimated output of R72 000 million in 2003/2004 (FAO, 2005). With 80% of SA's land surface being classified as semi-arid to arid, the application of fertilisers is a necessity to maintain food production (FAO, 2005). According to the Agricultural Research Counsel in SA, the ideal time to apply fertilisation is at the start of the rainy season, before rainfall reaches a maximum (ARC-Grain Crops Institute, 2013).
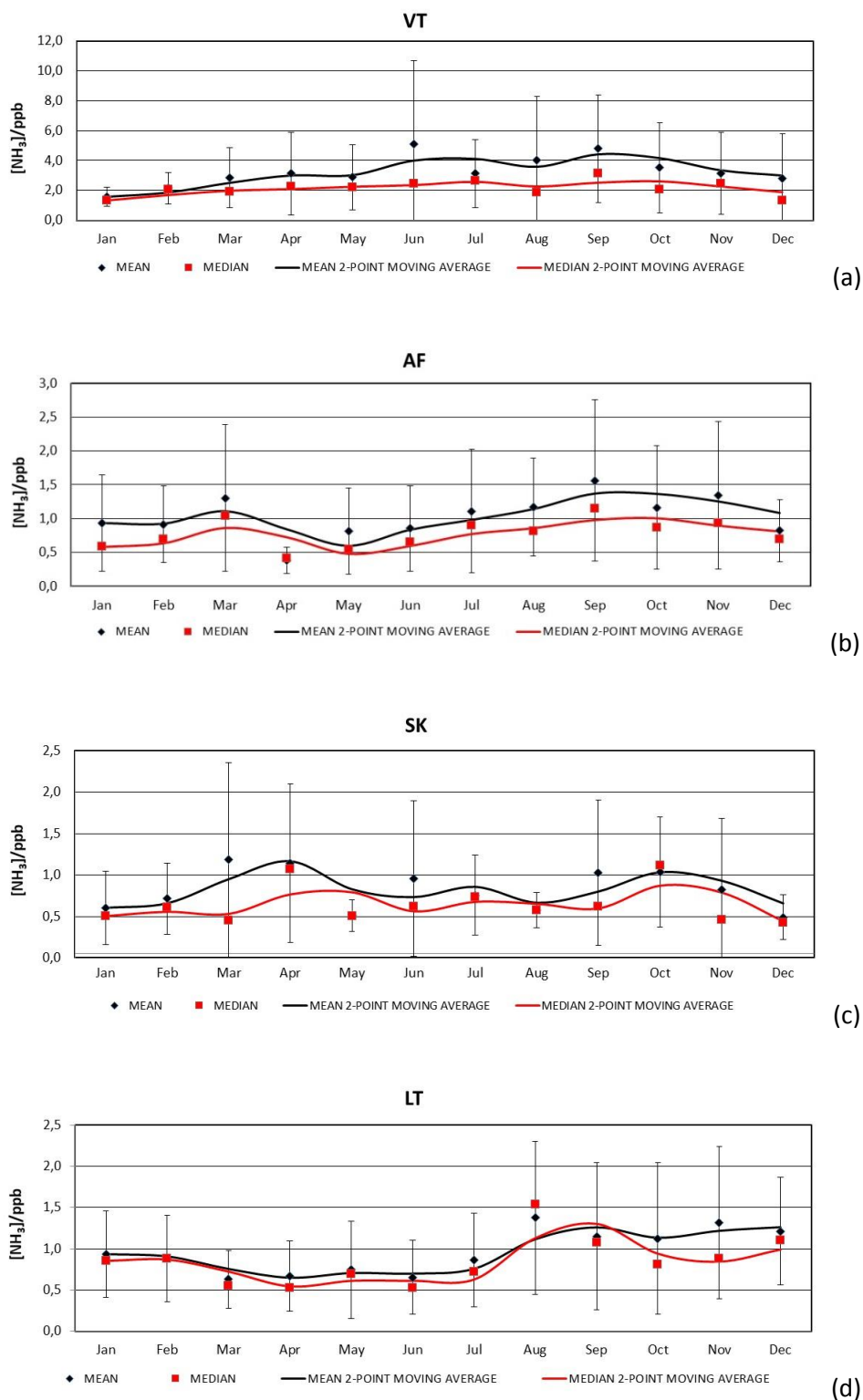
Figure 3.18: Monthly average concentrations of NH₃ for the total period at (a) Vaal Triangle; (b) Amersfoort; (c) Skukuza and (d) Louis Trichardt. The error bars indicate the standard deviation per month from all measurements over the entire study period.

3.3.4   Seasonal variations of HNO$_3$

Figure 3.19 shows the monthly average concentrations of HNO$_3$, calculated over the measurement period, i.e. from 2003 to 2012, with the exception of the VT site that ranged from 2008 to 2012, as mentioned previously. Although a clear seasonal trend is not evident, there is a slight increase in concentrations during spring (September-November) and summer (December-February), which coincides with the rainy season in the central and northern parts of South Africa. One of the formation pathways of HNO$_3$ is aqueous phase oxidation (refer to section 1.4.5), and consequently the onset of the rainy season could most likely attribute to the enhanced production of HNO$_3$. Another possible reason for the observed increase could be related to the enhanced photochemical activity of precursor gases (Adon *et al.*, 2010). NO$_2$ and NH$_3$ gaseous species also show increased concentrations during the wet season, as mentioned above. A correlation between NO$_2$ and HNO$_3$ might indicate a direct link between these two species in the atmospheric nitrogen cycle (refer to section 1.3.1 of this chapter).
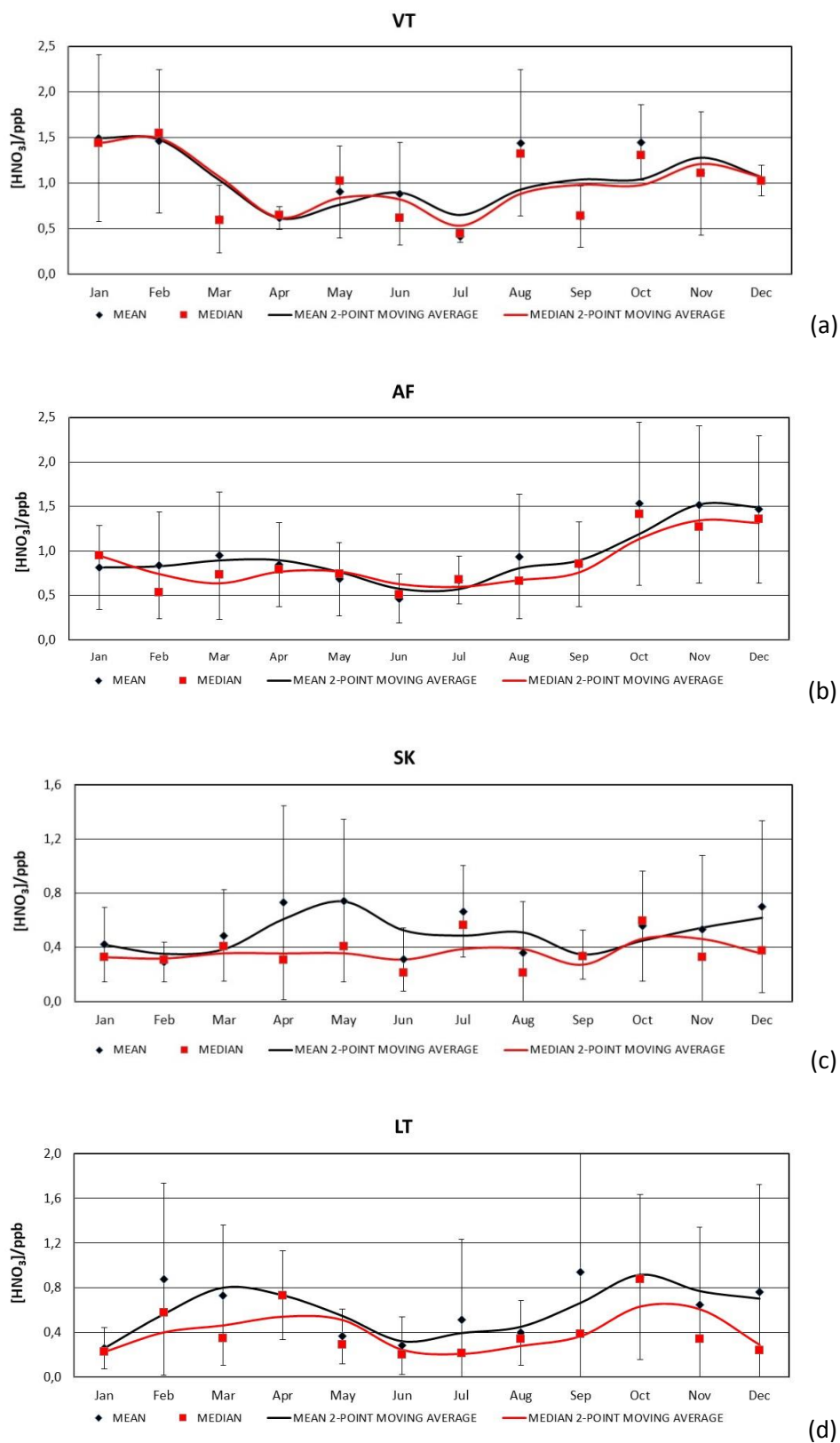
Figure 3.19: Monthly average concentrations of HNO₃ for the total period at (a) Vaal Triangle; (b) Amersfoort; (c) Skukuza and (d) Louis Trichardt. The error bars indicate the standard deviation per month from all measurements over the entire study period.

3.3.5 Seasonal variations of O_3

Monthly average values for O_3 (Figure 3.20) showed a definite seasonal influence, with ozone peaking during spring-time. This correlates well with earlier recorded observations by Martins *et al.* (2007) and similar observations made by Lourens *et al.* (2011) and Venter *et al.* (2012). This can most likely be attributed to a number of factors, such as prevailing stable atmospheric conditions (observed during winter months) at the start of spring and the longer days that result in increased photochemical activity in the form of photo-dissociation of NO_2 through solar radiation (Lourens *et al.*, 2011; Zunckel *et al.,* 2004). Since O_3 is a secondary air pollutant, the formation of O_3 from its precursor gases most likely occurs during air transport from the source regions. This could account for the differences between the O_3 seasonal pattern at VT (Figure 3.20 (a)) and the NO_2 seasonal pattern at VT (Figure 3.17(a)). The dominant transport pathway (Figure 3.2) of the precursor gases and gives it the necessary time needed for O_3 formation (Zunckel *et al.,* 2004).

Furthermore, it was observed that the most polluted sites (namely VT and AF) had lower monthly average concentrations due to the reactions that occur between O_3 and other pollutant species. It was also observed that the higher humidity at SK resulted in lower O_3 concentrations (Figure 3.20 (c)), since it is known that an inverse relationship exists between O_3 and H_2O.
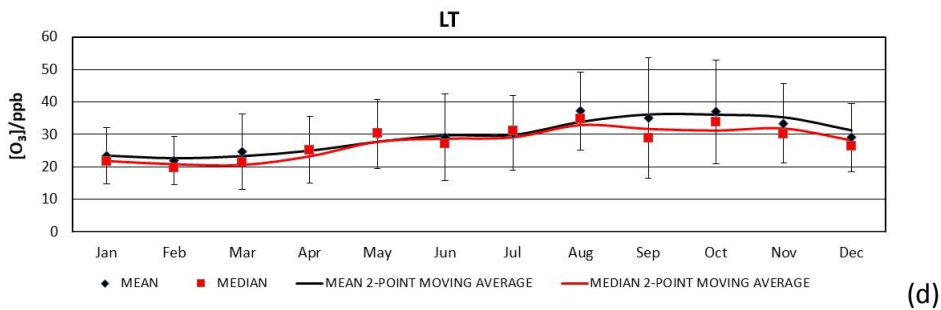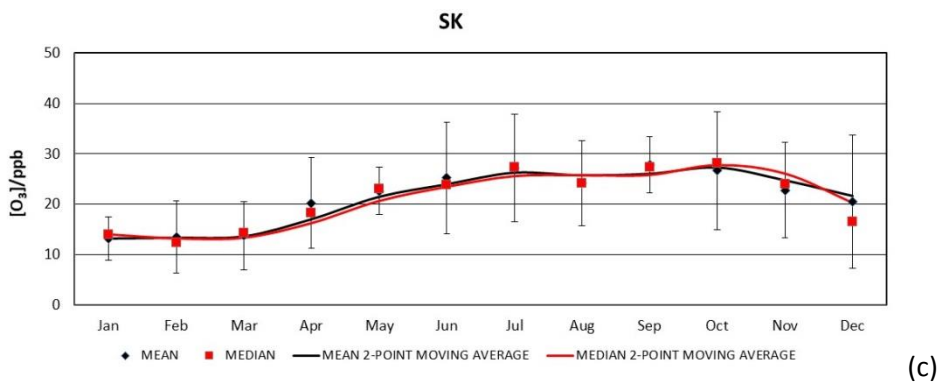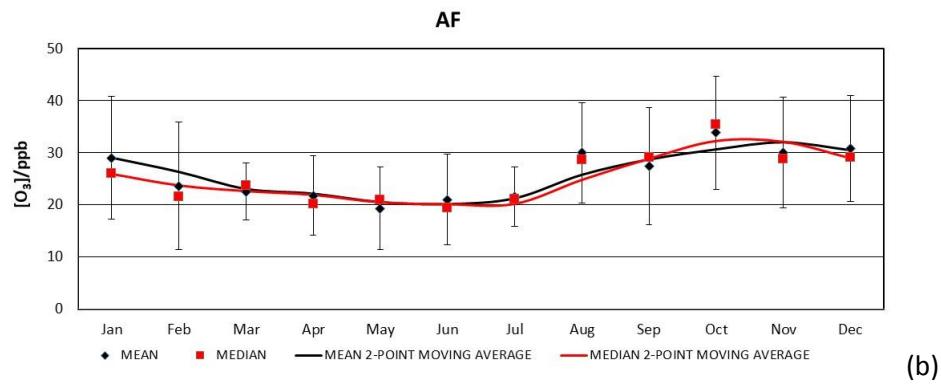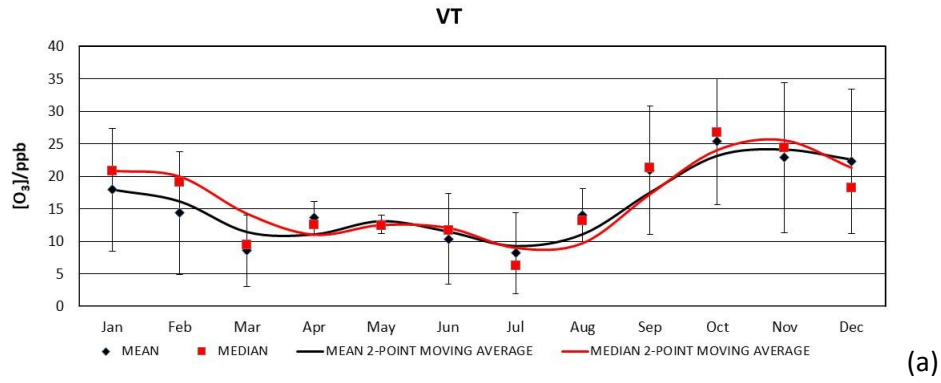
Figure 3.20: Monthly average concentrations of O₃ for the total period at (a) Vaal Triangle; (b) Amersfoort; (c) Skukuza and (d)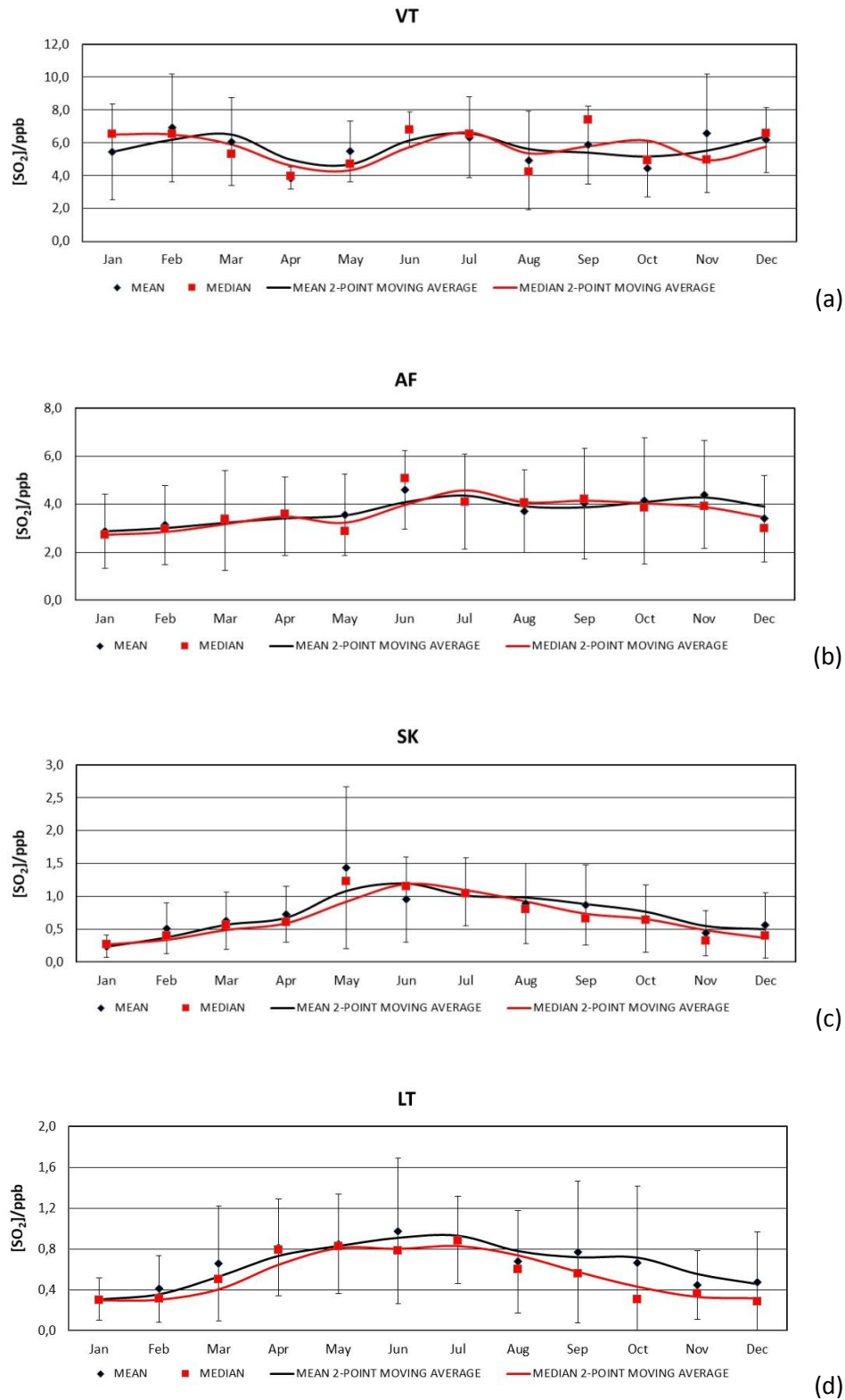 Louis Trichardt. The error bars indicate the standard deviation per month from all measurements over the entire study period.

4 Conclusions

Passive samplers were successfully deployed at SA DEBITS sites to measure monthly averages of atmospheric concentrations of SO_2, NO_2, NH_3, O_3 and HNO_3, with 90% of all samplers deployed resulting in usable results. The data illustrates the value and necessity of long-term air quality measurements at background sites.

The influence of a country's environmental policies and global awareness and focus on air pollution/prevention could be seen from a reduction in emissions of S and N pollutant gases up to 2003/2004, as well as the influence of socio-economic growth and international trade (international accreditation). The rapid industrial, economic and consumption growth in SA from 2002 to 2004 resulted in an increase in the emissions of gases. This was followed by the global financial crisis in 2007/2008 that influenced the production of large companies in SA, resulting in observed declines in the concentrations of gaseous species. Since 2010 a more pronounced increase was observed in the annual average concentrations at all sites. The increases can be attributed to high economic growth rates, which did not compensate for certain improvements, such as the incorporation of more stringent legislative application and electrification of informal settlements.

The meteorological synopsis of South Africa generally leads to the concentration of gaseous species, as well as the circulation of pollutant species via the dominant anti-cyclonic high pressure cell mostly during the dry winter months. The transport of pollutant species was confirmed by back-trajectory analysis and was observed in the declining trend of gaseous concentrations measured at each site along the anti-cyclonic pathway. Another contributing factor was investigated, namely the changes in air mass circulation from one year to the next, indicating that slight changes in the direction from where the air masses originated could have a significant impact on the measured concentrations of trace gases at the different sites.

Throughout the result section, it was evident that anthropogenic activities dominated at two sites, namely VT and AF, influencing the concentrations measured at these sites and indicating the impact of the industrial sector (e.g. coal-fired power generation, petrochemical industry and transport) on the country. The other two sites, SK and LT, showed more regional influences and indicated the effect of meteorological conditions on measurements (e.g. the anti-cyclonic circulation of pollutants from the two industrial sites).

NH_3 and NO_2 annual average concentrations showed similar increases in 2011. One possible reason was linked to increased occurrences of veld fires in 2011. However, the NH_3 levels at the VT site

were four times higher in 2011 compared to 2010, while NO_2 concentrations were only one and a half times higher. This led to the conclusion that the industrial activities in the Vaal Triangle, which are strongly linked to NH_3 emissions, caused this increase as well as the increase in NO_2 since NH_3 can be converted to NO_2. Tourism affected measurements in SK; for instance, the higher traffic volumes compared to LT accounted for differences in NO_2 concentrations between these two sites. NH_3 had high inter-annual variations when compared to other studies conducted in Africa. This could most likely be attributed to the substantial increase that was observed in 2011, affecting the percentage of the inter-annual variability.

The NH_3/SO_2 ratios were below 1 at the two industrially impacted sites (AF and VT) and just above 1 at the two regionally impacted sites (SK and LT), compared to values above 10 reported at other African sites (Adon *et al.*, 2010). This is indicative of the importance that SO_2 has, the strong influence it will have on the acidity potential of precipitation and in aerosol processes, as well as the more pronounced industrial influence in SA when compared to other African sites.

The short atmospheric lifetime of HNO_3 made it difficult to evaluate long-term trends and to draw comparisons to NO_2, which is the only source of HNO_3. However, the concentrations that were observed at the sites in this study correlated well with other sites in SA and the regional background sites, SK and LT, also compared well with other African studies.

The long-term trends of O_3 showed similar decreases up to 2001, as were observed for the other gaseous species, correlating with a decrease in production as the precursor gases decrease. South Africa is situated within the sub-tropical and temperate latitudes, with high levels of sunshine and high levels of precursor gases from the two pollutant priority areas. This is the ideal atmosphere for the formation of O_3 and, together with the unique climatology of SA, causes high levels of O_3 to be measured. The titration of O_3 by NO_x could also be observed at the sites in this study, where O_3 concentrations were highest at LT and lowest at VT, the inverse of what was observed for NO_2. Other contributing factors to the difference in O_3 concentrations were also taken into account, for instance the distance travelled from the precursor source areas that gives O_3 formation time to take place, as well as height above mean sea level and low humidity that could attribute to an increase in O_3 concentrations.

Annual total gaseous dry sulphur deposition (contributed by SO_2) was 4.6, 7.1, 1.0 and 0.9 kgS/ha/a at AF, VT, SK and LT, respectively, correlating well with the recent global assessment (Vet *et al*., 2014). Annual total gaseous dry nitrogen deposition (contributed by NO_2, NH_3 and HNO_3) was 9.7, 3.8, 2.2 and 2.1 kgN/ha/a at VT, AF, SK and LT, respectively. Deposition estimates were higher than

modelled observations in the recent global assessment (Vet *et al*., 2014) at VT (especially for NO_2, which was estimated at 2-4 kgN/ha/a for Southern Africa), both VT and AF were much higher compared to other African sites (Delon *et al*., 2010; Adon *et al*., 2013). This might be due to the strong industrial anthropogenic influence experienced at South African sites, but the deposition velocities used in this study might also contribute to higher deposition estimates. Furthermore, it must be emphasised that bidirectional exchange was not taken into account and only the downwards deposition was considered. It is also known that deposition velocities are associated with large uncertainties. This might alter the final deposition values quite significantly for species such as NO_2, NH_3 and HNO_3. Values for SO_2 and O_3 are not as strongly influenced by emissions from biota and soils, although different meteorological conditions might have an impact on these values and on the deposition velocities used.

The meteorological conditions of SA, with high-pressure anti-cyclonic circulation, lower PBL and the formation of inversion layers causes a trapping and concentrating of pollutants during the cold, dry winter months (May-September) that strongly influences the seasonal patterns observed for the trace gases. Seasonal variations for pollutant species measured in this study were not very clear at sites impacted by industry, possibly due to the local emissions that dominate the measurements.

Increases in SO_2 concentrations were observed during the colder months that are linked to the increased use of household combustion for cooking and heating purposes and lower inversion layers.

NO_2 showed a gradual increase throughout the winter up to the end of winter – also linked to increased household combustion and more natural veld fires as the dry season progresses, as well as a clear seasonal maximum in early spring that can be attributed to soil denitrification at the start of the growing season and consequently an increase in soil moisture. The VT site showed a definite mid-winter increase, possibly linked to the trapping of pollutants from the dominant industrial emissions in this region due to the unique climatology of SA.

The seasonal pattern of NH_3 showed two different cycles. The first is observed for the two industrially influenced sites at VT and AF, where an increase in the winter is observed due to the trapping and concentration of pollutants due to the climatology in SA, as described in section 3.3. The second observed cycle shows an increase at the start of the rainy season, possibly indicating an increase in microbial activity as the soil moisture increases (Delon *et al.*, 2012). Other major emission sources (Vet *et al.*, 2014) are the decomposition of urea in animal excreta, emissions from soils

(Schlesinger and Hartley, 1992), savanna fires (Delmas *et al.,* 1991; Brocard *et al.*, 1996) and the application of fertiliser (FAO, 2005; ARC-Grain Crops Institute, 2013).

HNO_3 showed increases during the rainy season, and is possibly linked to the enhanced photochemical activity of precursor gases and aqueous phase HNO_3 production. A correlation between NO_2 and HNO_3 might indicate a direct link between these two species in the nitrogen cycle.

O_3 showed a definite seasonal influence with it peaking during spring-time. This could be attributed to numerous factors such as the prevailing stable atmospheric conditions at the start of spring and longer days resulting in enhanced photochemical activity due to biomass burning and other precursors.

The current study compared well with other studies conducted in South Africa. Measurements of SO_2 and NO_2 clearly divided the sites of the current study into two groups. The regional sites (SK and LT) correlated well with other studies on the African continent, while VT (and to a lesser extend AF) compared to measurements from China. NH_3 levels were low compared to other African sites and most of the other international sites used in the comparison. HNO_3 levels were also higher than other African sites, which could be linked to the short atmospheric lifetime that limits the trans-boundary pollution transport and the higher level of NO_2 available for the formation of HNO_3 at SA sites. Ozone concentrations on a regional scale compared high with other African sites, which could be attributed to regional characteristics, sunlight and 'natural' veld fires.

Chapter 3

Chapter 4: Assessment of precipitation chemistry and wet deposition

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In this chapter, the chemical composition and wet deposition determined for rain samples collected at all four the sites from 2009 to 2014 are presented and discussed, as well as a comparison to previous precipitation chemistry reported at these sites. These sites are considered to be regionally representative of the north-eastern interior of South Africa. Two of these sites are in the region where the major anthropogenic emission sources in South Africa are situated. The annual volume weighted mean indicated that the concentration of anthropogenically associated species was much higher at the two sites that are in close proximity to anthropogenic activities, while the concentrations of maritime and terrigenous species were higher at the two sites not directly impacted by major anthropogenic sources. Back trajectory analysis, however, did indicate that these two remote sites are also impacted by air masses passing over the source region through anti-cyclonic recirculation. In general, increases in the wet deposition of S and nitrogen (N) were observed at all the sites compared to previous results reported. In addition, an increase in the H⁺ concentration is observed at all the sites that are reflected in pH distributions indicating more rain events with lower pH values. This could be ascribed to a significant increase in anthropogenic activities and population growth in this part of South Africa with an associated increase in energy demand.

The results given in this chapter has been published in Atmospheric Environment (Conradie, et al., 2016)

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1 Introduction

The chemical composition of rainwater reflects various interacting physical and chemical mechanisms in the atmosphere, which include emission and source amplitude, atmospheric transport processes, atmospheric chemical reactions and removal processes (Lacaux *et al.*, 2009). Precipitation chemistry also gives a general picture of changes in the composition of the atmosphere caused by anthropogenic activities, as well as changes in meteorology and climate (Vet *et al.*, 2014). The importance of the chemical composition of wet deposition as a source of nutrients, i.e. nitrogen (N), sulphur (S), carbon (C) and base metals, is widely recognised (Duce *et al.*, 2009), while precipitation could also be a source of toxic species. Although it can be a very difficult task, it is important to establish atmospheric budgets of key chemical compounds to understand the functioning of ecosystems and biogeochemical cycles (Dentener *et al.*, 2006, Davidson *et al.*, 2012). Vet *et al.* (2014) recently presented a comprehensive global assessment on precipitation chemistry and the deposition of biogeochemical important species, which emphasised the importance of wet deposition measurements.

Acid rain was identified in the 1960s as a problem when impacts were observed on aquatic ecosystems and forests (Möller, 1999), acidification of the environment (Gorham, 1998), as well as damage to buildings and sculptures (Ozga *et al.*, 2011; Dolske, 1995). Wet deposition delivers acid and acidifying compounds to the surface of the earth, which adversely affect soil, vegetation, coastal waters and continental waters (Bravo *et al.*, 2000). The main cause of this human-induced environmental problem has been the emission of S and N compounds into the atmosphere from sources such as energy production, transport, industry and agriculture. A global assessment of rainwater pH performed in 2002 by utilising models estimated that Europe, China and eastern North America had the lowest pH values (Rodhe *et al.*, 2002), which was attributed mainly to higher sulphate concentrations. However, nitric acid has also increasingly become an important contributor to the acidity of rainwater in many regions of China and North America (Xiao, 2016).

The potential adverse environmental impacts related to increased anthropogenic emissions into the atmosphere necessitate the execution of long-term atmospheric measurement programmes. Comprehensive assessments on air quality (Monks *et al.*, 2009) and atmosphere-biosphere interactions (Fowler *et al.*, 2009) indicated the importance of long-term atmospheric chemistry measurements. From these assessments, important current and emerging policy requirements could be identified, as well as the need for appropriate data to address related research questions (Vet *et al.*, 2014).

South Africa is regarded as an important source region of biogeochemical and anthropogenic atmospheric pollutants. An intense NO_2 hotspot is clearly visible over the South African Mpumalanga Highveld (Lourens *et al.*, 2012), with the borders of the Mpumalanga province indicated in Fig. 2.7 of Chapter 2. South Africa is also regarded at the 9th largest atmospheric S-emitting country (Stern, 2006), while biomass burning (wild fires) plumes from this area are known to affect Australia and South America (Wenig *et al.*, 2003). Maritz *et al.* (2014) also indicated the significant influence of biomass burning on the concentrations of atmospheric organic compounds. Furthermore, South Africa is regarded as the economical hub of southern Africa. Notwithstanding the importance of South Africa and the need for long-term monitoring programmes, very limited data has been published on the chemical composition of precipitation for this region (Laakso *et al.*, 2012).

Mphepya *et al.* (2004; 2006) reported on the precipitation chemistry of samples collected at three South African sites, i.e. an industrially influenced site (Amersfoort) and a rural background site (Louis Trichardt) in South Africa from 1986 to 1999, as well as a site at Skukuza in the Kruger National Park from 1999 to 2002. These studies estimated that the chemical composition of precipitation at these sites is controlled by mainly five source groups, i.e. marine, terrigenous, nitrogenous, biomass burning and anthropogenic (fossil fuel) sources. Due to logistical reasons, wet precipitation collection did not continue beyond the above-mentioned periods at South African IDAF sites. However, the collection of rain events recommenced in 2009 and is currently on-going. In this chapter, the chemical composition and wet deposition determined for precipitation samples collected from 2009 to 2014 at four South African IDAF sites are presented and discussed. The results of the samples collected in 2009 to 2014 are also compared to the precipitation chemistry reported by Mphepya *et al.* (2004; 2006). Furthermore, the influence of anthropogenic activities in South Africa on wet deposition at remote sites will also be discussed.

2   Calculations and statistical evaluations

The annual volume weighted mean (VWM) in $\mu eq.L^{-1}$ of each ion was calculated using the following equation (Laouali *et al.*, 2012; Mphepya *et al.*, 2004, 2006; Galy-Lacaux *et al.*, 1998):

$$\text{VWM } (\mu eq.L^{-1}) = \sum_{i=1}^{N} c_i p_i \Big/ \sum_{i=1}^{N} p_i \tag{1}$$

Where c_i is the ionic concentration of each ion in $\mu eq.L^{-1}$, p_i is the rainfall depth (mm) and N is the total number of samples with valid ionic concentrations for a specific ion. The total number of samples (N) that were used to calculate the VWM for each site is presented in Table 4.2. The H^+ concentrations were calculated from the measured pH values. The annual wet deposition (WD),

expressed in kg.ha^{-1}.yr^{-1}, was calculated by multiplying the annual VWM with the total annual rainfall depth at each site and the molar mass (equivalent weight) of the specific ion. The mean WD for the six year sampling period was calculated by using the average annual rainfall from 2009 – 2014 of each of the sites presented in Table 4.2. The total annual precipitation amount includes all rain events in the year and not only the events used to calculate the VWM as specified by the WMO precipitation chemistry guidance manual (WMO GAW, 2004).

The contribution of sea salt to the chemical composition of precipitation is commonly estimated by calculating the excess concentrations of K^+, Mg^{2+}, Ca^{2+}, Cl^- and SO_4^{2-} with respect to sea salt using N^+ as a reference. Keene *et al.*, (1986) presented reference ratios of these species with regard to Na^+ in seawater. The sea salt fractions of any of these species, X, with respect to Na^+ is:

$$[X]_{marine} = [Na^+]_{rain} \text{ x } [X / Na^+]seawater \tag{2}$$

Where $[X]_{marine}$ is the sea salt contribution of X in $\mu eq.L^{-1}$, $[Na^+]rain$ is the concentration of Na^+ in rain ($\mu eq.L^{-1}$) and $[X / Na^+]seawater$ is the seawater concentration ratio (Keene *et al.*, 1986).

The non-sea salt fraction of X can then be calculated by:

$$[X]_{nss} = [X]_{rain} - ([Na^+]_{rain} \text{ x } [X / Na^+]_{seawater}) \tag{3}$$

Where $[X]_{rain}$ is the concentration of element X in rainwater, and $[X]_{nss}$ is the non-sea salt contribution of element X in $\mu eq.L^{-1}$. The enrichment factors (EF) with regard to the reference X / Na^+ ratio were calculated by (Quiterio *et al.*, 2004; Chao and Wong, 2002):

$$EF_x = [X / Na^+]_{rain} / [X / Na^+]_{marine} \tag{4}$$

Where EF_x is the enrichment factor of element X and $[X / Na^+]_{rain}$ is the ratio of element X with regards to Na^+ in precipitation. EFs must be evaluated carefully since EFs are considered to be a simplified method to determine the marine contribution to precipitation composition (Reimann *et al.*, 2005).

In the South African context, SO_4^{2-} can be viewed as a reference ion for anthropogenic activities. After subtracting the marine contribution (calculated by using Equation 3), the excess SO_4^{2-} can be attributed either to the terrigenous or anthropogenic pollution. The contribution of anthropogenic sources to SO_4^{2-} in rain water can be inferred by assuming that the SO_4^{2-} contribution from terrigenous sources is in excess of that supplied by gypsum (Delmas, 1981). Thus, the anthropogenic SO_4^{2-} contribution can be calculated using the following equation (Delmas, 1981):

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$$[SO_4^{2-}]_{anthropogenic} = [SO_4^{2-}]_{nss} - 0.47 [Ca^{2+}]_{nss} \tag{5}$$

Sulphuric acids, nitric acids and organic acids together can be defined as the acidic potential (Laouali *et al.*, 2012). Neutralisation of sulphuric and nitric acids by bases that consists of base cations (e.g. Mg^{2+}, Ca^{2+} and NH_4^+) and anions (e.g. carbonates and bicarbonates) can be evaluated by calculating the neutralisation factors (NF) with the following equation (Laouali *et al.*, 2012, Possanzini *et al.*, 1988):

$$NF_X = X / (NO_3^- + SO_4^{2-}) \tag{6}$$

Where X is the base cation of interest, i.e. Mg^{2+}, Ca^{2+} and NH_4^+.

Statistical evaluations, i.e. principal component analysis (PCA) and Spearman correlations were performed with MATLAB programming software. PCA were performed in order to identify similar possible sources of chemical species that influence the chemical composition of rain water samples, while correlations between chemical species could also indicate similar origin and/or the same transported air masses.

3 Results and discussion

3.1 Summary of collected samples and annual rainfall for the study period

Table 4.1 presents the total number of samples collected and chemically analysed, as well as the number of samples that passed the WMO ID% criteria and collected samples discarded due to analytical errors or not being of sufficient volume for complete analyses. The number of wet deposition samples collected included all the events for which the rain depth was measured. All these rain events had rain depths of more than 0.2 mm. According to exposure sheets received with each of the wet deposition samples, no incidences were reported where collected wet deposition samples had to be excluded due to instrumental or operational failures during the entire sampling period. Furthermore, exposure sheets also indicated that all the wet deposition samples collected represent a single rain event and do not contain an accumulation of several rain events. The number of samples that did not have sufficient volumes for complete analysis were 1, 8, 8 and 20 at AF, VT, LT and SK, respectively. The percentage of samples that passed the WMO ID% criteria and were not discarded due to analytical errors listed in Table 4.1 represents wet deposition samples that were in the WMO percentage total precipitation (%TP) acceptance range, i.e. the %TP is the percentage of the total rainfall depth measured that was associated with valid precipitation chemistry data.

Table 4.1 Summary of samples collected at South African IDAF sites in 2009 – 2014

	Amersfoort							Vaal Triangle						
Year	2009	2010	2011	2012	2013	2014	2009-2014	2009	2010	2011	2012	2013	2014	2009-2014
Number of events collected (*N*)	55	60	49	50	63	46	323	88	93	73	70	60	61	445
Number of events not passing the WMO ID% criteria	6	13	14	13	5	0	51	15	19	21	6	1	4	66
Number of events discarded due to analytical errors	0	0	0	0	1	1	2	1	1	0	2	4	0	8
Collected rainfall	696	767.4	426	431.75	743.25	736	3800.4	793	954.5	607	815.5	754.1	1222	5146.1
Total rainfall	720	912	576	613.25	821.25	736	4378.5	895.5	1083	818	901	814.1	1227	5738.6
Average rainfall							729.75							956.43
% TP	96.67	84.14	73.96	70.40	90.50	100	86.80	88.55	88.13	74.21	90.51	92.63	99.58	89.68

Site	Louis Trichardt							Skukuza						
Year	2009	2010	2011	2012	2013	2014	2009-2014	2009	2010	2011	2012	2013	2014	2009-2014
Number of events collected (*N*)	31	25	32	20	20	29	157	42	49	45	29	50	42	257
Number of events not passing the WMO ID% criteria	9	1	8	2	0	0	20	1	8	3	0	1	0	13
Number of events discarded due to analytical errors	0	0	1	5	2	0	8	2	3	2	9	4	0	20
Collected rainfall	775	492	469.5	352	754.7	985.5	3828.7	604.5	582.5	451.8	443	749.3	492	3323.1
Total rainfall	901.5	504	696.5	482	799.7	985.5	4369.2	611.8	616.6	522.8	474.4	781.8	492	3499.4
Average rainfall							728.2							583.23
% TP	85.97	97.62	67.41	73.03	94.37	100	87.63	98.81	94.47	86.42	93.38	95.84	100	94.96

Number of events collected during 2009 – 2014 at all the sites	1182	Number of events discarded due to analytical errors	38
Number of events not passing the WMO ID% criteria during 2009 – 2014 at all the sites	150	%TP	89.77

In Figure 4.1 the precipitation events for AF, VT, LT and SK for the sampling period, as well as the total annual rainfall depths are presented. These rain depths were measured with standard funnel rain gauges at each of the selected sites, which were recorded by the site operators after a single

rain event occurred. Therefore it is assumed that the percentage precipitation covering length (%PCL) is 100% where %PCL is the percentage of rain event depths measured with the rain gauge (WMO, 2004). From these figures the strong seasonality of rainfall is evident at all of the sites, with most precipitation occurring between mid-spring – early autumn. Annual precipitation ranged between 576 – 912 mm at AF, 818 – 1227 mm at VT, 482 – 985.5 mm at LT and 474.5 – 782 mm at SK. Relatively large inter-annual rainfall variability is observed at AF and LT. Annual rainfall at SK was relatively constant, with the exception of 2013 that had higher annual rainfall compared to previous years, while the annual rainfall at VT were comparable for all five years.
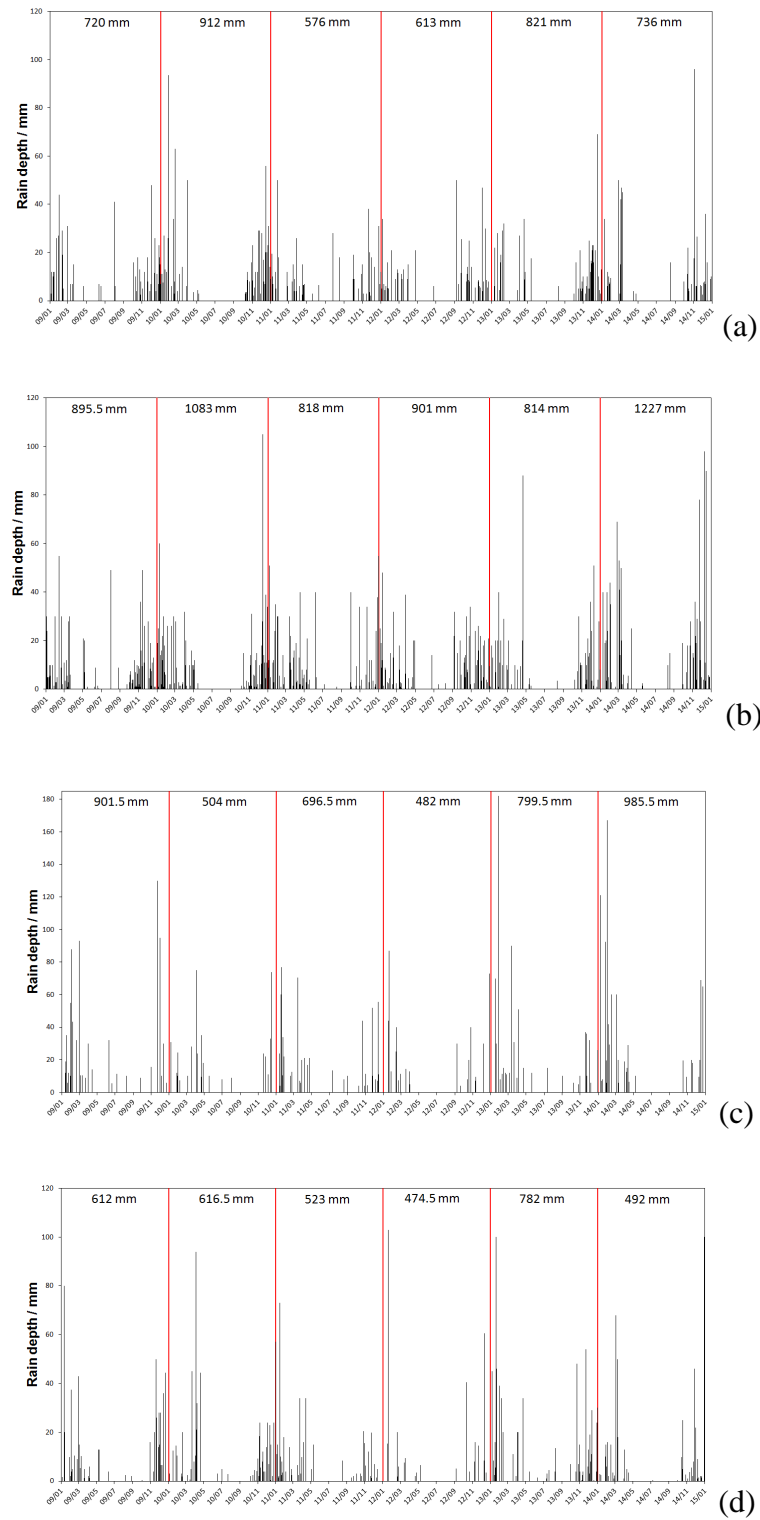
Figure 4.1: Precipitation events at AF(a), VT(b), LT(c) and SK(d) occurring during the period 01/01/2009-31/12/2014. The annual rainfall depth for each year is indicated at the top of each figure

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3.2 Ionic composition and acidity of wet deposition

The VWM ionic concentrations and fluxes of wet deposition, as well as the averaged pH and averaged electrical conductivity (EC) values determined at all the IDAF sites in the interior of South Africa from 2009 to 2014 are presented in Table 4.2. The VWM concentrations of COO^-, CH_3COO^-, $C_2H_5COO^-$ and $C_2O_4{}^{2-}$ were combined, which are presented as a total for water-soluble OA.

The precipitation at AF and VT was dominated by $SO_4{}^{2-}$. Since S emissions in southern Africa are mostly attributed to anthropogenic activities, it is evident that these activities have a major influence on the atmospheric chemical processes in the region. The reported values of $SO_4{}^{2-}$ at VT and AF are much higher than that reported for other sites in Africa (Galy-Lacaux *et al.,* 2009) and, with the exception of eastern North America, eastern Europe and East Asia, even higher than most other regions in the world (Vet *et al.,* 2014).

The second and third most abundant species at AF were $NO_3{}^-$ and $NH_4{}^+$, respectively. These two species were also the second and third most abundant species at VT with $NH_4{}^+$ levels being higher than $NO_3{}^-$. Similar to $SO_4{}^{2-}$, $NO_3{}^-$ and $NH_4{}^+$ concentrations were also higher (2 – 3 times) at AF and VT than at LT and SK. This may also reflect that AF and VT were more affected by anthropogenic emissions. However, since the difference is smaller for $NO_3{}^-$ and $NH_4{}^+$ compared to that of $SO_4{}^{2-}$, it also indicates that more source groups contribute to the concentrations of $NO_3{}^-$ and $NH_4{}^+$ than to the $SO_4{}^{2-}$ concentrations at the different sites. The significantly higher VWM concentrations of $SO_4{}^{2-}$ and $NO_3{}^-$ measured at AF and VT are in accord with NO_2 and SO_2 concentrations being higher at AF and VT than at LT and SK (see Chapter 3). The second most abundant species at LT was OA, which is an indicator of biomass burning.

Table 4.2: VWM, average annual WD and pH of precipitation at the South African IDAF sites from 2009-2014

	Amersfoort		Vaal Triangle		Louis Trichardt		Skukuza	
	2009 – 2014		2009 – 2014		2009 – 2014		2009 – 2014	
	VWM / µEq/L	WD / kg.ha^{-1}.yr^{-1}	VWM / µEq/L	WD / kg.ha^{-1}.yr^{-1}	VWM / µEq/L	WD / kg.ha^{-1}.yr^{-1}	VWM / µEq/L	WD / kg.ha^{-1}.yr^{-1}
pH	4.32		4.51		4.89		4.66	
EC	42.6		33.6		13.1		22.9	
H^+	61.18	0.45	44.64	0.43	15.24	0.11	22.24	0.13
Na^+	17.79	2.98	3.50	0.77	7.75	1.30	13.17	1.77
NH_4^+	28.50	3.75	29.06	5.01	10.85	1.42	12.80	1.35
N in NH_4^+		*2.91*		*3.89*		*1.11*		*1.04*
K^+	7.35	2.10	1.41	0.53	5.12	1.46	2.08	0.48
Mg_2^+	5.54	0.49	4.55	0.53	1.93	0.17	3.27	0.23
Ca_2^+	16.39	2.40	16.18	3.10	6.25	0.91	4.69	0.55
NO_3^-	33.40	15.11	22.97	13.62	7.49	3.38	13.20	4.77
N in NO_3^-		*3.41*		*3.08*		*0.76*		*1.08*
Cl^-	17.96	4.65	4.52	1.53	10.83	2.80	15.73	3.25
SO_4^{2-}	67.21	23.56	55.00	25.27	12.37	4.33	18.66	5.23
S in SO_4^{2-}		*7.87*		*8.44*		*1.44*		*1.75*
OA	14.64	5.57	12.51	6.10	12.14	4.54	9.69	2.93
OA*	13.24		11.49		11.10		8.69	

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It is also evident that AF and VT, the two sites closer to anthropogenic emissions, had lower average pH values (4.32 and 4.51, respectively) and higher H^+ concentrations (61.18 and 44.64 µEq/L, respectively), while LT and SK had higher mean pH values (4.89 and 4.75, respectively) and lower VWM H^+ concentrations (15.24 and 22.24 µEq/L, respectively). Table 4.2 shows that the average pH values at all the sites were in the range of 4.32-4.89, much lower than 5.60, which is the pH of unpolluted rainwater in equilibrium with atmospheric carbon dioxide (CO_2). The observed acidity is mainly due to the large influence of NO_x and SO_2 industrial emissions on the industrialised Mpumalanga Highveld and the Vaal Triangle, as well as organic acid contributions from biomass burning that is being re-circulated over the interior of South Africa (Laouali *et al.*, 2012; Laakso *et al.*, 2012; Tyson *et al.*, 1996). Average pH values determined at the South African IDAF sites are much lower compared to the pH of rainwater in western African countries where the acidity is predominantly associated with organic species from emitted biogenic processes and biomass burning, with calcium carbonate/bicarbonate acting as a major buffering agent for acidity in rain (Galy-Lacaux *et al.*, 2009; Laouali *et al.*, 2012). These values are also lower than the average global values reported by Vet *et al.* (2014) and are therefore clearly influenced by anthropogenic activities in southern Africa.

The pH frequency distributions at the four South African IDAF sites are presented in Fig. 4.2. Although the pH distribution of individual wet deposition rain events were quite different among the four sites, over 94% of rain events observed at each site had pH lower than 5.60. At AF, 17% and less than 1% of rain events had pH <4.00 and >6.00, respectively. The largest number of rain events had pH values between 4.0 and 4.4 at AF. The highest frequency of rain events was at VT at pH values between 4.2 and 4.6, while 10.2% of rain events had pH values lower than 4.0 and 0.8% were higher than 6.00. At LT, the pH values of individual rain events ranged predominantly between 4.4 and 5.0. 1.5% of rain events at LT were below 4.0, while 2.2% were higher than 6.0. 4% of rain events at SK were lower than 4.0 and 0.9% were higher than 6. The largest number of rain events had pH values ranging between 4.4 and 5.0.
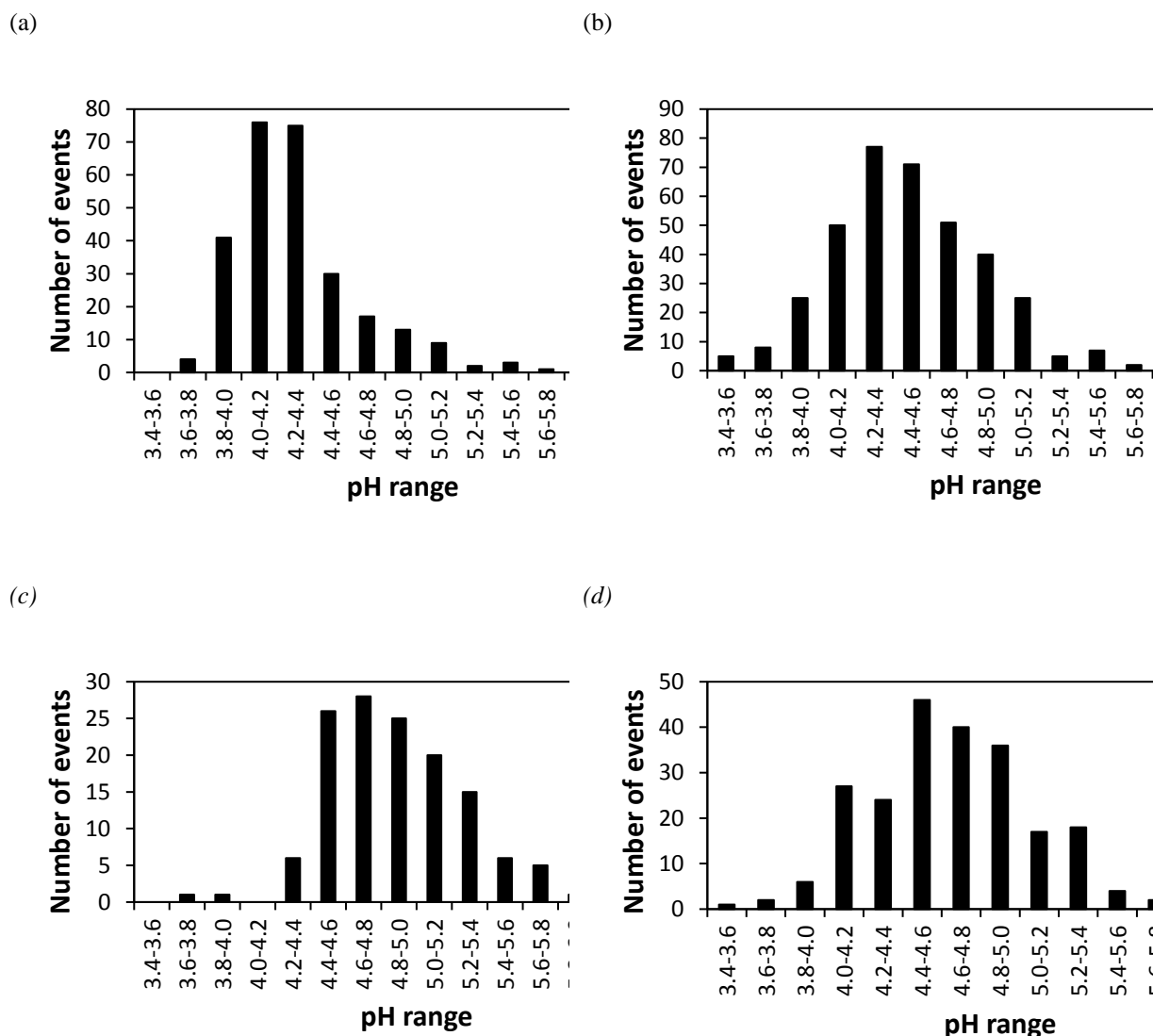
Figure 4.2: pH event distribution graphs for 2009-2014 at AF (a), VT (b), LT (c) and SK (d)

The acidity potential (pA) can be defined as the sum of the potential acidic compounds, i.e. sulphuric acid (anthropogenic SO_4^{2-}), nitric acid (NO_3^-) and organic acids (OA) (Mphepya *et al.*, 2004; Laouali *et al.*, 2012), which is presented in Table 4.3. The measured acidity (H^+, measured) at all the sites is considerably less than the total H^+ concentration estimated, which can be attributed to neutralisation. NFs can be calculated to evaluate the neutralisation of sulphuric and nitric acids by bases consisting of cations (e.g. Ca^{2+}, NH_4^+ and Mg^{2+}) associated with anions (e.g. oxides, carbonates) by using Equation 7, which are presented in Table 4.4 for the four sites. It is evident that NH_4^+ is the major ionic species present in wet deposition that neutralises the strong acids, with Ca^{2+} being the second most important species. Mphepya *et al.* (2004) and Mphepya *et al.* (2006) also attributed the lower pA compared to measured acidity to neutralisation.

Table 4.3 Contributions of the mineral and organic acids to the total acidity

	AF 2009 - 2014		VT 2009 - 2014		LT 2009 - 2014		SK 2009 - 2014	
	$\mu eq.L^{-1}$	%	$\mu eq.L^{-1}$	%	$\mu eq.L^{-1}$	%	$\mu eq.L^{-1}$	%
Sulphuric acid	56.8	55	54.5	61	7.6	29	15.1	41
Nitric acid	33.7	32	23.0	26	7.5	29	13.2	36
Organic acids	13.1	13	11.5	13	11.1	42	8.7	23
Total H^+, estimated (pA)	103.5	100.0	89.0	100.0	26.2	100.0	37.0	100.0
H^+, measured	61.2	56	44.6	50	15.2	58	22.2	61

Table 4.4 Neutralisation factors (NFs) of acidic rainwater calculated for each of the South African IDAF sites for 2009-2014

Site	NF_{Ca2+}	NF_{Mg2+}	NF_{NH4+}
Amersfoort	0.19	0.07	0.32
Vaal Triangle	0.21	0.06	0.38
Louis Trichardt	0.41	0.13	0.72
Skukuza	0.17	0.12	0.45

The calculated potential contribution of the mineral acids (sulphuric and nitric acid) at AF and VT is 84% and 87%, respectively, which forms the greatest part of free acidity at these sites affected by industrial and other anthropogenic activities. The potential contribution of mineral acids also dominated wet deposition collected at SK, which contributed 77% of the free acidity, indicating the impacts of air masses passing over the industrialised Mpumalanga Highveld (Fig. 3.2, Chapter 3). Although the potential contribution of mineral acids at LT was 58%, a much larger contribution of organic acids, i.e. 42% was calculated at LT, which can partially be attributed to the larger relative contribution of biomass burning at LT.

3.3 Wet deposition fluxes of ions

The wet deposition fluxes of the species determined at the four sites correspond with the relative concentrations of these species in the wet deposition, i.e. species with higher VWM concentrations had higher wet deposition fluxes. The wet deposition flux of S was seven to eight times higher at AF (7.87 kg ha^{-1} yr^{-1}) and VT (8.44 kg ha^{-1} yr^{-1}) compared to depositions thereof at LT (1.44 kg ha^{-1} yr^{-1}) and SK (1.75 kg ha^{-1} yr^{-1}). The total wet deposition flux of N was approximately three times higher at AF (6.32 kg ha^{-1} yr^{-1}) and VT (6.97 kg ha^{-1} yr^{-1}) than total wet N deposition at LT (1.87 kg ha^{-1} yr^{-1}) and SK (2.12 kg ha^{-1} yr^{-1}). N is considered to be an important source of nutrients in ecosystems, while levels above a certain critical load, which depends on the specific ecosystem, can be considered to be contributing to pollution and eutrophication of the environment (Josipovic *et al.*, 2011).

3.4 Sources of ionic species

3.4.1 Principle component analysis (PCA) and correlations of ionic species

Linkages between different chemical species and similar sources can be statistically explored by performing principal component analysis (PCA) and Spearman correlation calculations, which are presented in Fig. 4.3. PCA was applied as an explorative tool in this study. From a statistical perspective the datasets were not large enough for definitive source apportionment with PCA. For PCA, the dataset was subjected to Box-Cox transformation in an effort to eliminate some possible artefacts, e.g. auto-correlations. There are no well-defined rules for the number of factors to be retained. In general, factors that are either meaningful or with eigenvalues larger than one are kept (Hosiokangas *et al.*, 1999). Three meaningful factors were determined for AF and VT, while two meaningful factors were determined for LT and SK. The factors identified explained 83.3%, 85.7%, 78.8% and 65.9% of the variances of the datasets for AF, VT, LT and SK, respectively.
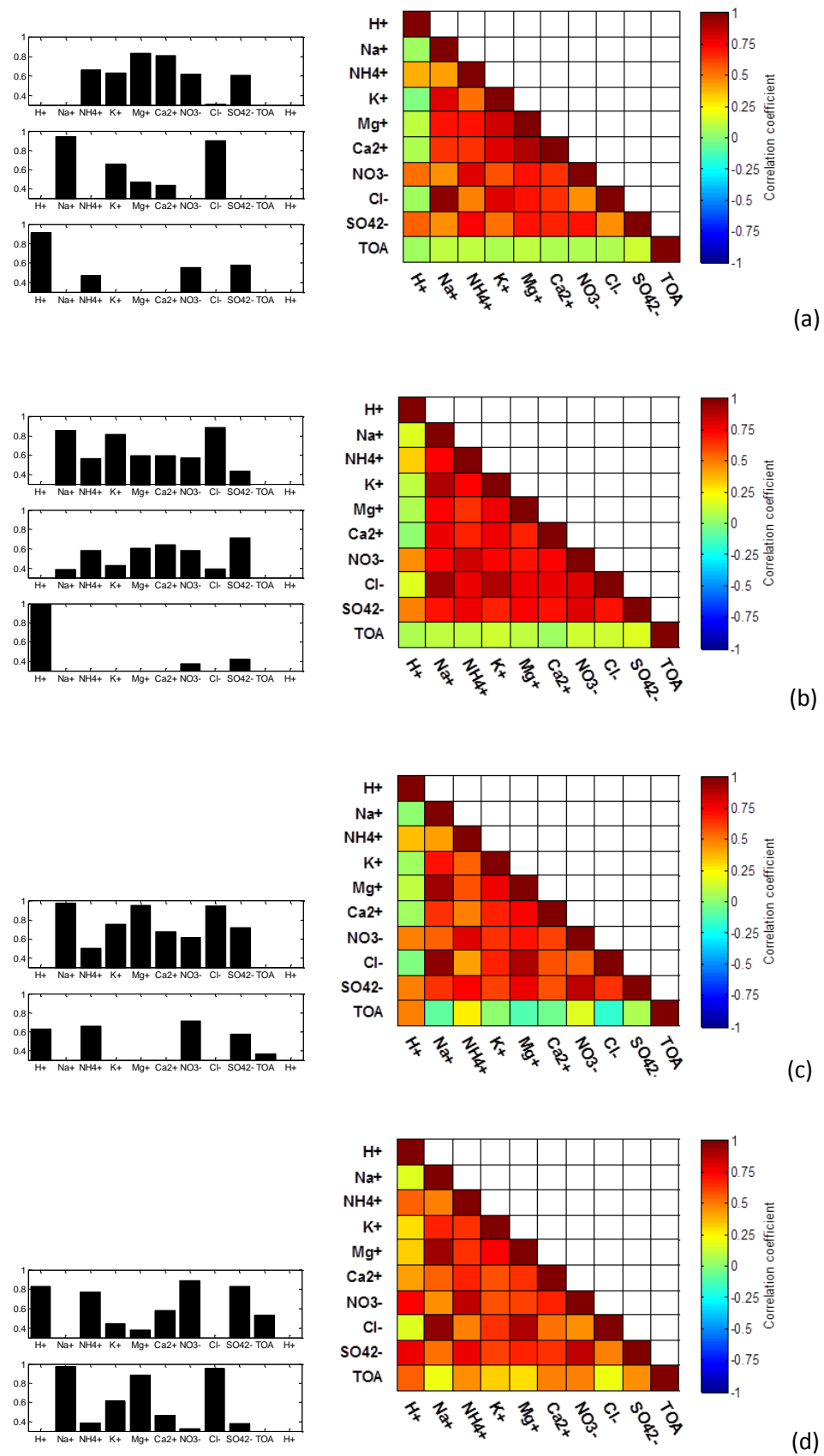
Figure 4.3: Principle component analysis (PCA) and Spearman correlation determined at (a) AF, (b) VT, (c) LT and (d) SK for the period 2009-2014

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Based on the results of PCA and Spearman correlation analyses, the main sources influencing the wet deposition composition at AF included terrigenous (crustal), marine, fossil fuel combustion and agricultural sources. The first PCA factor is loaded with all the ionic species normally associated with terrigenous (crustal) sources. The second PCA factor includes Na^+ and Cl^- that are linked to a marine source, which is also strongly indicated by the Spearman correlation between these two ions. The third factor is associated with the acidity (H^+), which is expectedly related to known anthropogenic species (NH_4^+, NO_3^- and SO_4^{2-}) for this region, which is related mainly to fossil fuel combustion and agricultural activities. These linkages are also supported by the Spearman correlations between H^+ and these species. The contribution from biomass burning is not evident from these statistical analyses. Surprisingly, no correlation for OAs was indicated by either of these two methods.

The PCA analysis for VT yielded a more complex result. While it is clear from the third PCA factor that the acidity at VT is strongly associated with NO_3^- and SO_4^{2-}, the first and second factors seem to represent mixtures of marine, terrigenous (crustal) and fossil fuel sources. The Spearman correlations are slightly more indicative of different sources. At VT, the acidity is also strongly correlated with NO_3^- and SO_4^{2-}, while a weaker relation to NH_4^+ is observed as indicated by Spearman correlations. The strong Spearman correlation between Na^+ and Cl^- is again evident. The difficulty in separating signals from different sources at this site is expected, since this site is surrounded by different industries and other diverse anthropogenic sources.

For LT and SK, PCA analysis resulted in only two identifiable factors. One of these factors included ionic species associated with marine and terrigenous (crustal) sources (factor 1 at LT and factor 2 at SK), with the strong marine influence at these two sites reflected in this factor. The second factor was associated with the acidity and fossil fuel combustion and agricultural sources (factor 2 at LT and factor 1 at SK). The OAs are at both these sites well correlated with the acidity, which was not the case for AF and VT. This is indicative of the relevant importance of OAs from biomass burning in Africa to acidity at sites that are not strongly influenced by anthropogenic sources.

In addition to identifying different source regions, evidence for the neutralisation of acidic species, as discussed in section 3.2, is also provided by the good Spearman correlations between SO_4^{2-} and NO_3^-, and the cations Ca^{2+}, NH_4^+ and Mg^{2+}, as well as the correlations between these acidic ions and cations obtained with PCA as indicated in Fig. 4.3.

In combination, from these different calculations and correlations, the major source groups identified were marine, terrigenous (crustal), fossil fuel combustion, agriculture and biomass burning. The contributions to the chemical content of deposition and the atmospheric chemical characteristics of wet deposition will be explored in the following section.

3.4.2   Source contributions

Equations 3 and 4 in section 2 were used to estimate the marine (sea-salt fraction) and non-marine (non-sea-salt fraction) contributions for Ca^{2+}, SO_4^{2-}, Mg^{2+}, K^+, and Cl^-. An estimation of these source contributions was calculated by assuming Na^+ was completely of marine origin. The non-marine contributions for Ca^{2+}, Mg^{2+}, K^+ and Cl^- were considered to be terrigenous (crustal), while the non-marine SO_4^{2-} was divided into terrigenous and anthropogenic source contributions with the two methods described in section 2. Furthermore, it can be assumed that anthropogenic sources of SO_4^{2-} are predominantly fossil fuel combustion in this part of South Africa. NO_3^- and NH_4^+ can be associated with different sources, which include anthropogenic sources and biogeochemical processes. At the West African IDAF sites, NO_3^- and NH_4^+ could mainly be associated with natural sources (Galy-Lacaux *et al.*, 2009). However, it can be assumed for the South African IDAF sites that NO_3^- is predominantly associated with fossil fuel combustion, while NH_4^+ is mainly related to agriculture. The biomass burning contribution could be related to OA VWM concentrations. In Fig. 4.4, a summary of the estimations of the source group contributions to the chemical content of wet deposition at South African IDAF sites is presented.

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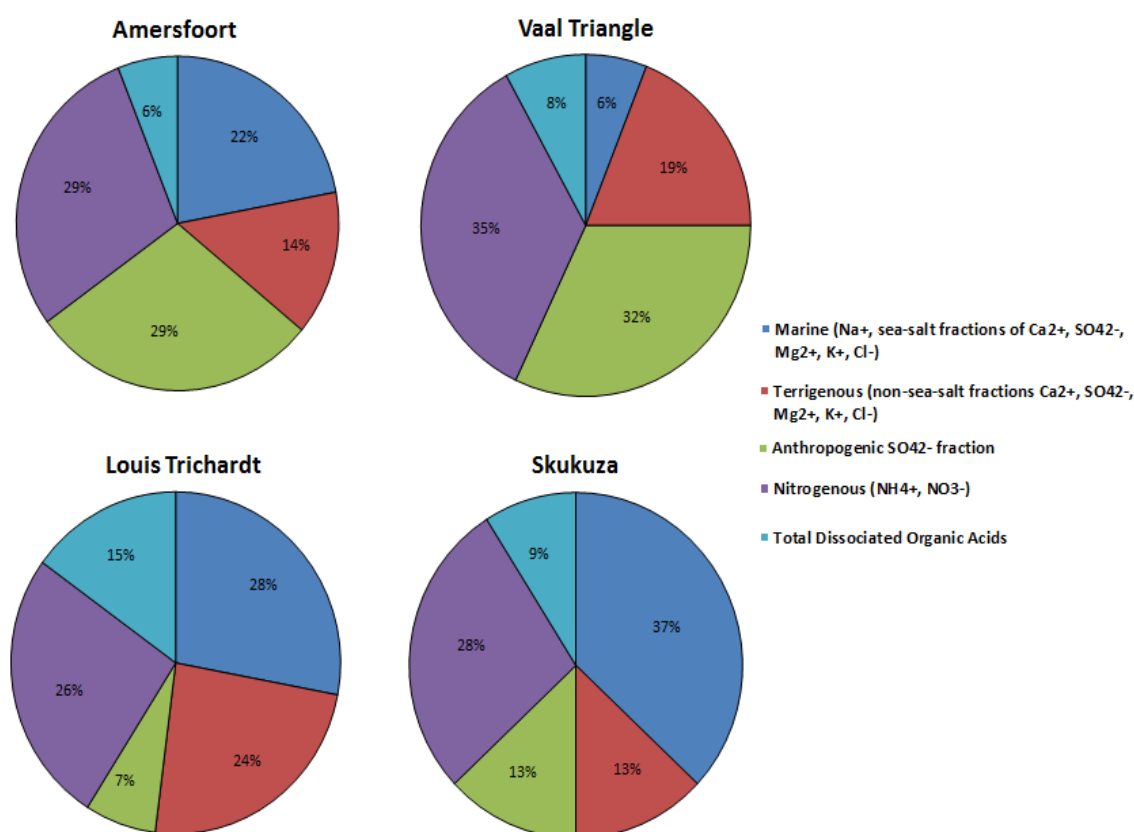
Figure 4.4: Estimations of contributions to the chemical content of precipitation at the SA IDAF sites

3.4.2.1 Marine contributions

In Table 4.5, the ratios of K^+, Mg^{2+}, Ca^{2+}, Cl^- and SO_4^{2-} in relation to Na^+ are presented. In addition, the EFs calculated with Equation 5 with regard to the reference seawater ratios, according to Keene *et al.* (1986), are also listed. The Cl^-/Na^+ ratios at all the sites were close to the seawater ratio (1.161), with the EFs being close to 1. In addition, a strong correlation is observed between Na^+ and Cl^- at all the sites (Fig. 4.3). Since southern Africa is surrounded by the Atlantic and Indian Oceans, the oceans can be considered to be the major sources of Na^+ and Cl^-.

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Table 4.5: Comparison of rainwater and seawater ratios and corresponding enrichment factors (EF) at the respective sites for the period 2009 to 2014

Ions	Seawater*	Amersfoort 2009 – 2014	Vaal Triangle 2009 – 2014	Louis Trichardt 2009 – 2014	Skukuza 2009 – 2014
Ca^{2+} / Na^+	0.044	0.895	4.627	0.806	0.356
EF $_{(Ca2+)}$		20.4	105.4	18.4	8.1
SO_4^{2-} / Na^+	0.121	3.429	15.727	1.595	1.417
EF $_{(SO42-)}$		28.3	130.0	13.2	11.7
Mg^{2+} / Na^+	0.227	0.308	1.302	0.249	0.248
EF $_{(Mg2+)}$		1.4	5.7	1.1	1.1
K^+ / Na^+	0.022	0.412	0.404	0.660	0.158
EF $_{(K+)}$		17.8	18.3	30.0	7.2
Cl^- / Na^+	1.161	1.002	1.291	1.397	1.194
EF $_{(Cl-)}$		0.9	1.1	1.2	1.0

*Seawater ratios from Keene *et al.,* 1986

It also indicates that marine air masses affect all the sites, as indicated by overlay back trajectories (Fig. 3.2, Chapter 3), especially at LT, SK and AF. The Mg^{2+}/Na^+ ratios were also close to that of seawater (0.227) at LT and SK, with strong correlations observed between Na^+ and Mg^{2+}, and Cl^- and Mg^{2+} at these two sites. This indicates that the ocean is also a strong source of Mg^{2+} at these sites. The lesser marine influence at AF and, especially, VT is reflected by the Mg^{2+} / Na^+ ratio being higher than the seawater ratios thereof. The relatively weaker correlation between Na^+ and Mg^{2+}, and Cl^- and Mg^{2+} at these two sites compared to the correlations thereof at LT and SK also supports this conclusion. The much higher Mg^{2+} at VT might be attributed to the proximity of several large pyro

metallurgical smelters (Fig. 2.7, Chapter 2), since it is well known that fly ash of such smelters has elevated levels of Mg. The higher Mg^{2+} at AF can also be ascribed to being regionally affected by large point sources as indicated in Fig. 2.7, Chapter 2 and Fig. 3.2, Chapter 3.

The marine contribution to the various sites was calculated according to the VWM concentrations and the ratio of Na^+ to the various other ions in seawater (using the ratios from Keene *et al.*, 1986 in Table 4.5), from the data listed in Tables 4.2 and 4.5 by determining the sum of the marine contributions in relation to the total ionic content at the sites (e.g.($[Na^+]+[K^+]+[Mg^{2+}]+[Ca^{2+}]+[Cl^-]+[SO_4^{2-}]$)seawater/ [Total VWM ionic concentrations]). From these calculations, the marine contribution during the study period was estimated to be 22% at AF, 6% at VT, 28% at LT and 37% at SK (Fig. 4.4).

3.4.2.2 *Terrigenous (crustal) contributions*

The terrigenous (crustal) contribution to the chemical composition of wet deposition is linked to African soil dust species, e.g. calcite, dolomite, gypsum and other key minerals such as illite, smectite and palygorskite. In wet deposition, the correlations between Ca^{2+}, Mg^{2+} and SO_4^{2-} are used as an indication of this source strength. These species are relatively well correlated at all the sites, as indicated in Fig. 4.3. Soil dust is considered to be a major constituent of the regional aerosol load of the South African atmosphere (Piketh *et al.*, 1999; Van Zyl *et al.*, 2014), which can originate from natural soil erosion or dust emitted from industrial activities. Mphepya *et al.* (2004) also indicated that an additional source of Ca^{2+} and SO_4^{2-} at South African IDAF sites, especially at AF, could be coal combustion. Coal combustion is a major source of SO_4^{2-}, while Ca is a major element in fly ash (Mahlaba *et al.*, 2011).

The terrigenous (crustal) contributions to each of the sites were calculated by subtracting the marine contributions from the total VWM concentrations, while an anthropogenic contribution was additionally subtracted for SO_4^{2-}. The sum of the terrigenous (crustal) contributions in relation to the total ionic content (e.g. ($[K^+] + [Mg^{2+}] + [Ca^{2+}] + [Cl^-] + [SO_4^{2-}]$) terrigenous / [Total VWM of ionic concentrations])) could then be determined. The terrigenous (crustal) contributions to the total ionic content during the study period were estimated to range between 14 and 15%, 15 and 19%, 19 and 24%, and 9 and 13% at AF, VT, LT and SK, respectively, depending on the method applied to calculate the anthropogenic SO_4^{2-} contribution (source contributions presented in Fig. 4.4 were based on calculations from the second method). Terrigenous (crustal) sources contribute relatively significantly to the chemical composition of wet deposition in southern Africa. This is not surprising,

since southern Africa is a semi-arid region in which rainfall is mostly associated with convective events.

3.4.2.3 *Fossil fuel combustion contributions*

SO_4^{2-} in wet deposition results from emissions of gaseous sulphur dioxide (SO_2) (and hydrogen sulphide (H_2S) to a lesser extent) and particulates containing SO_4^{2-}. In the north-eastern interior of South Africa, where the South African IDAF sites are situated, SO_2 and SO_4^{2-} are primarily emitted through anthropogenic activities, i.e. fossil fuel combustion (coal-fired power stations and petrochemical plant) and biomass burning (household combustion). As described previously, the non-marine SO_4^{2-} was divided into terrigenous and anthropogenic (fossil fuel combustion) source contributions with two methods described in section 2, i.e. estimating anthropogenic SO_4^{2-} by calculating the excess of that supplied by gypsum (Equation 6) and a method where a baseline SO_4^{2-} concentration is subtracted from the total SO_4^{2-} VWM concentration. These results are presented in Table 4.6.

Table 4.6: Estimation of SO_4^{2-} sources in $\mu eq.L^{-1}$. Terrigenous and anthropogenic values in brackets were calculated with the second method (assumption of background concentration of 7 $\mu eq.L^{-1}$), while the other terrigenous and anthropogenic values were calculated with the first method (excess of that supplied to gypsum).

Site	Total/µEq/L	Marine/µEq/L	Non-marine / µEq/L	
			Terrigenous	Anthropogenic
Amersfoort	67.2	2.2	7.3(4.8)	57.7(60.2)
Vaal Triangle	55.0	0.4	0.1(6.6)	54.5(48.0)
Louis Trichardt	12.4	1.0	2.6(6.0)	8.9(5.4)
Skukuza	18.7	1.6	2.0(5.4)	15.1(11.7)

It follows from Table 4.6 that the estimated anthropogenic contribution to SO_4^{2-} concentrations in wet deposition is approximately 86, 99, 72 and 80% at AF, VT, LT and SK, respectively as calculated with Equation 6. The second method, where the global background concentration of 7 $\mu eq.L^{-1}$ was subtracted from the total SO_4^{2-} VWM concentrations, estimated that 90, 87, 43 and 62% of the SO_4^{2-}

at AF, VT, LT and SK, respectively were of anthropogenic origin. The anthropogenic source contribution to SO_4^{2-} with these two methods differs somewhat for each of the sites and needs further exploration. Long-term tracer studies that quantify the anthropogenic contribution are probably the best methodology to follow. However, these types of studies are very expensive and not really feasible within the current sampling network. In terms of the present study, however, it is evident that both methodologies indicate a very strong anthropogenic influence on SO_4^{2-} at AF and VT of similar magnitude (~90%). The discrepancies between the two methods for LT and SK are probably related to an under-estimation of sources of gypsum at LT and VT.

NO_3^- is the final product of multiphase reaction processes of gaseous NO_x, atmospheric particles and cloud water (Galy-Lacaux *et al.*, 2009; Mphepya *et al.*, 2004). Gaseous NO_x is primarily emitted as nitrogen oxide (NO) from natural, e.g. biogenic emissions and biomass burning (naturally occurring wild fires), as well as anthropogenic sources, e.g. biomass burning (household combustion) and fossil fuel combustion (coal-fired power stations and vehicular emissions). However, according to reports on NO_2 emissions in this region from anthropogenic sources (Collette *et al.*, 2010; Lourens *et al.*, 2011; Pretorius *et al.*, 2015), it is expected that a relatively significant fraction of NO_3^- can be considered to be of anthropogenic origin, i.e. fossil fuel combustion emissions from coal-fired power, plants, petrochemical industries, traffic and household combustion.

The large impacts of fossil fuel combustion at AF and VT are evident from the large contribution of the fossil fuel combustion source groups indicated in Fig. 4.4, i.e. 44% at AF and 47% at VT. As mentioned before, the Vaal Triangle is a highly industrialised area with various large point sources (Fig. 2.7, Chapter 2). AF is situated in close proximity to the industrialised Mpumalanga Highveld where nine coal-fired power stations, a petrochemical plant and a number of pyrometallurgical smelters are located (Fig. 2.7, Chapter 2). In addition to these large point sources in the Mpumalanga Highveld, traffic emissions and household combustion also contribute to elevated levels of atmospheric pollution (Helas & Pienaar, 1996). The AF and VT sites are also situated in regions that have been declared national priority areas by the South African government, i.e. the Highveld Priority Area and the Vaal Triangle Air-shed Priority Area, respectively (Government Gazette, 2007; 2005). The declaration of these regions as priority areas indicates that they are relatively highly polluted by anthropogenic activities. Furthermore, AF is also ~200 km west from the Johannesburg-Pretoria conurbation with a population of more than 10 million people (Fig. 2.7, Chapter 2) (Lourens *et al.*, 2012). The 96-hour overlay back trajectories presented in Fig. 3.2, Chapter 3 for AF clearly indicate the impacts of air masses passing over the Johannesburg-Pretoria conurbation and the Mpumalanga Highveld with AF being frequently affected by air masses moving over the south-

eastern to north-eastern sector. The overlay back trajectories for VT (Fig. 3.2, Chapter 3) indicate that, in addition to local point sources in the Vaal Triangle, VT is also the affected by regional atmospheric pollution and the Johannesburg-Pretoria conurbation.

Although LT and SK have a smaller contribution from the fossil fuel combustion source groups (Fig. 4.4), overlay back trajectories for LT and SK (Fig. 3.2, Chapter 3) indicate that these sites are also affected by air masses moving over the strongly anthropogenically affected source regions. These overlay back trajectory patterns clearly demonstrate the general anti-cyclonic recirculation pattern of air masses over this part of southern Africa (Van Heerden & Taljaard, 2015). The concentration profile of species associated with fossil fuel combustion pollution also indicates that polluted air masses are diluted as the air masses travel further from the source region to SK and LT. This is reflected in the concentrations of SO_4^{2-} and NO_3^- being slightly higher at SK compared to LT (Table 4.2).

3.4.2.4   *Agricultural contributions*

Atmospheric NH_4^+ results from emissions of gaseous ammonia (NH_3) and particulates containing NH_4^+. The major sources of NH_3 include bacterial decomposition of urea in animal excreta and from natural or fertilised soils (Schlesinger & Hartley, 1992), wild fires and household combustion of wood (Delmas *et al.*, 1995; Broccard *et al.*, 1996). In addition, the production of fertilisers and petrochemical plants can also be considered a significant source of NH_3. It is evident from Fig. 4.4 that the agricultural source group contributions were similar at AF, LT and SK, which can be attributed to regional farming activities in the north-eastern interior of South Africa. A larger agriculture contribution is observed at VT, which is expected due to large scale industrial production of fertilisers in this area.

3.4.2.5   *Biomass burning contributions*

Biomass burning can be considered to originate from natural and anthropogenic sources. In these results, the concentrations of the total dissociated organic acids were used as a proxy for the contribution of biomass burning, i.e. wild fires. It is evident from Fig. 4.4 that the largest contribution of biomass burning was at LT. The widespread regional atmospheric influence of biomass burning in southern Africa is evident (Sinha, 2004) from the biomass burning source group estimations determined at all of the sites.

3.5 Inter-annual variability and seasonal variations

The total annual VWM concentrations and fluxes of the ten ions showed significant changes from 2009 to 2014 as indicated in Fig. 4.5. Over the 2009 to 2014 period, the total annual VWM concentrations of the ten ions at VT and LT changed quite significantly on an inter-annual basis, while they were fairly similar at SK. At AF the total ionic concentrations were similar from 2009 to 2013, with relatively higher concentrations during 2014. It was expected that rainfall depth and the proximity of anthropogenic sources should have a strong influence on the VWM ionic concentrations. However, it is not the case in this instance, since these sites represent in each of these circumstances an anthropogenic impacted and a remote site. It is clear that the total VWM ionic concentrations therefore depend on a large number of factors. This observation is supported by the comparable relatively low VWM ionic concentrations measured at VT in 2010 and 2011 despite 2010 being a wet year (1 083 mm) and 2011 being a relatively dry (818 mm) year. The total VWM ionic concentrations are in both instances lower compared to other years. The relatively dry year, 2011, at VT is characterised by a significantly larger VWM concentration for Ca^{2+} that could be ascribed to more soil dust during a dryer period. The larger VWM concentration for NH_4^+ for the same period and site is probably due to an anthropogenic source in the region that had a more pronounced influence during a dry period. In 2009, a significantly higher OA VWM concentration was determined at LT, which indicated that the site was more frequently affected by biomass burning events during that year. This also illustrates the inter-annual variability of sources affecting the South African IDAF sites. The relatively large contribution of Na^+ and Cl^- to the total VWM ionic concentrations at SK in 2012 can likely be attributed to increased frequency of cold fronts – more specifically the ridging anticyclones that follow directly behind the cold fronts, from the southern oceans passing over South Africa from the south-west during the winter months as mentioned in Chapter 2.

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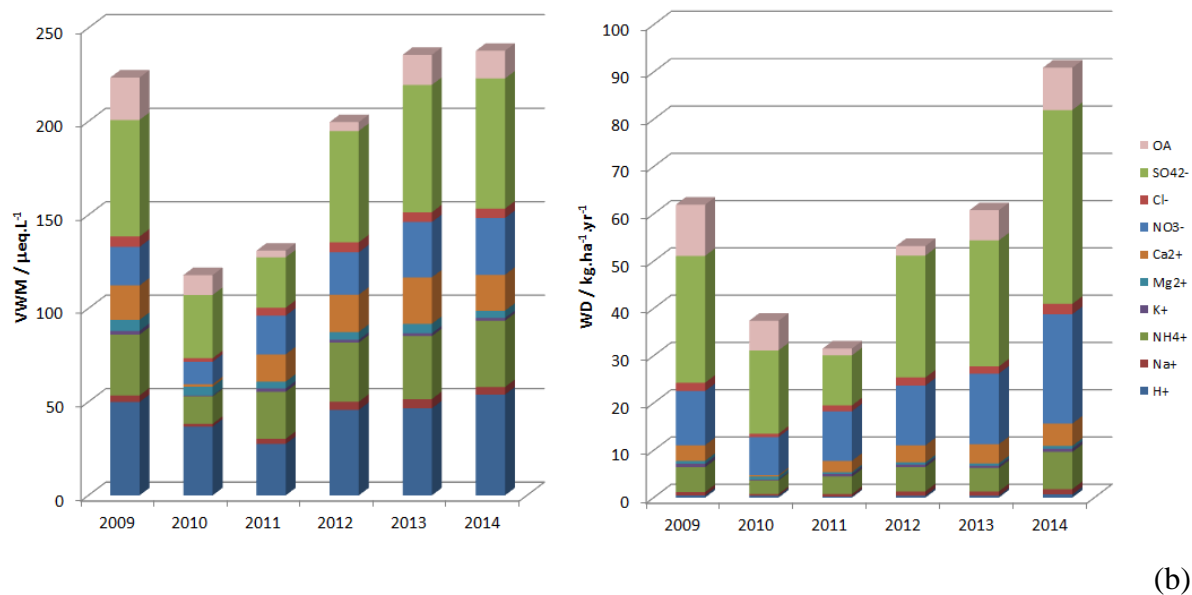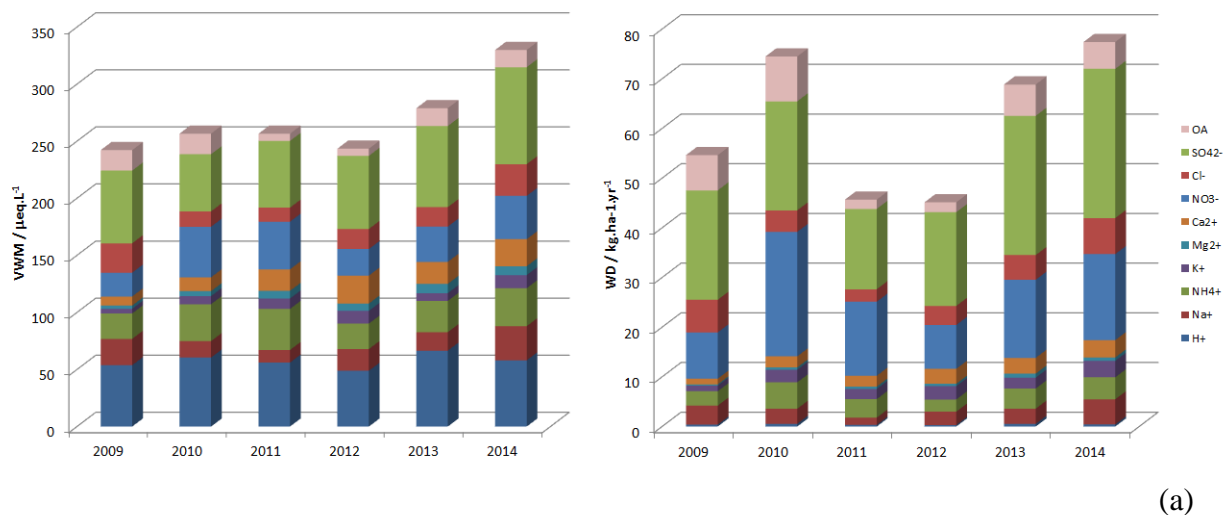
Figure 4.5: The contribution of the individual ions in rainwater to the total VWM and WD values at the different sites; (a) AF, (b) VT, (c) LT and (d) SK

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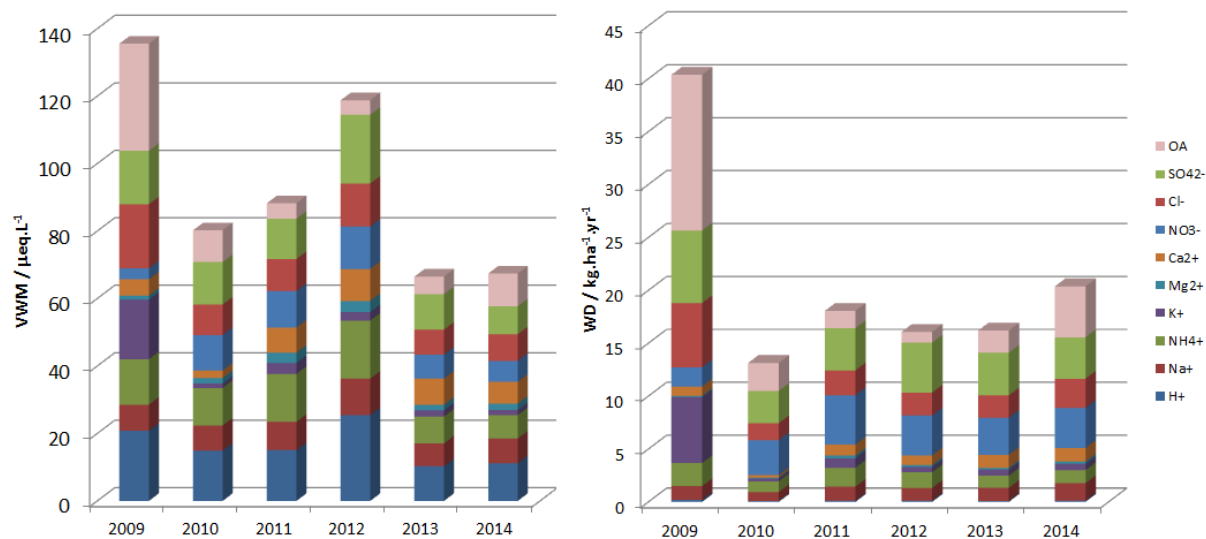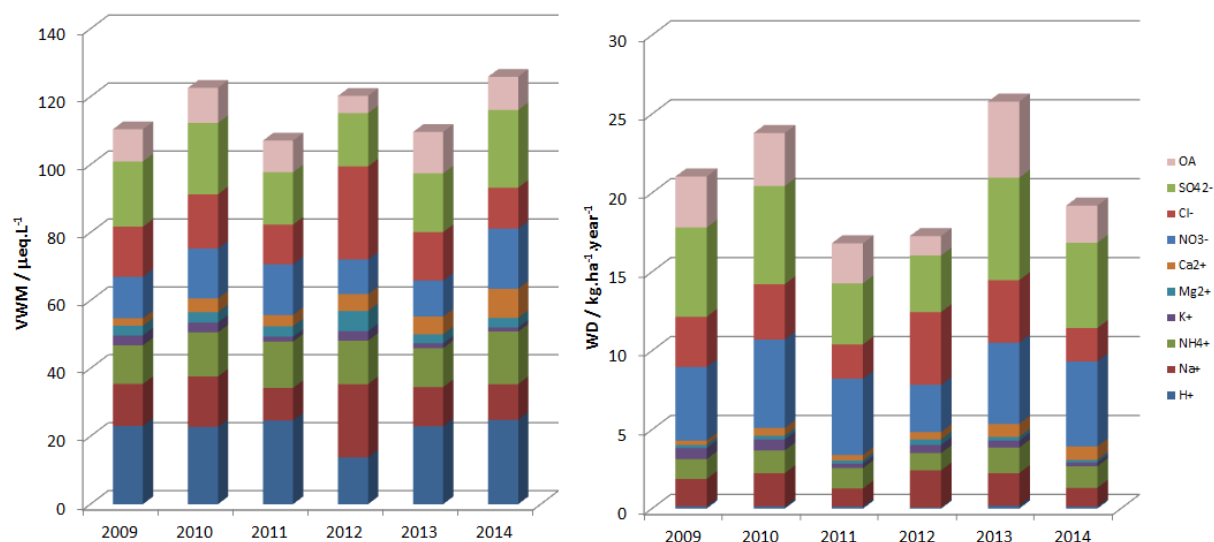
Figure 4.5 (continued): The contribution of the individual ions in rainwater to the total VWM and WD values at the different sites; (a) AF, (b) VT, (c) LT and (d) SK

From Fig. 4.5, it follows that the rainfall depth plays a very important role on the wet deposition fluxes, which is illustrated by the inter-annual wet deposition fluxes' variability correlating with the inter-annual changes in rainfall depth. Furthermore, it is evident that, although the four sites are from a global perspective relatively in close proximity, large inter-annual variations in the ionic concentrations and fluxes of wet deposition occur between these sites, which emphasises the importance of a good spatial coverage when establishing regions that are environmentally at risk. The wet deposition fluxes show inter-annual differences of up to 300% (e.g. at VT when comparing

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the total wet deposition fluxes in 2010 and 2014), which is mainly due to large fluctuations in the rainfall depth.

It is expected that the chemical composition of wet deposition would be different for each of the seasons due to the meteorological and environmental changes such as rainfall depth, land cover, vegetation growth, biomass burning and anthropogenic activities (e.g. more household combustion for space heating during colder months). The seasonal variability is presented in Fig. 4.6.

(a)

(b)
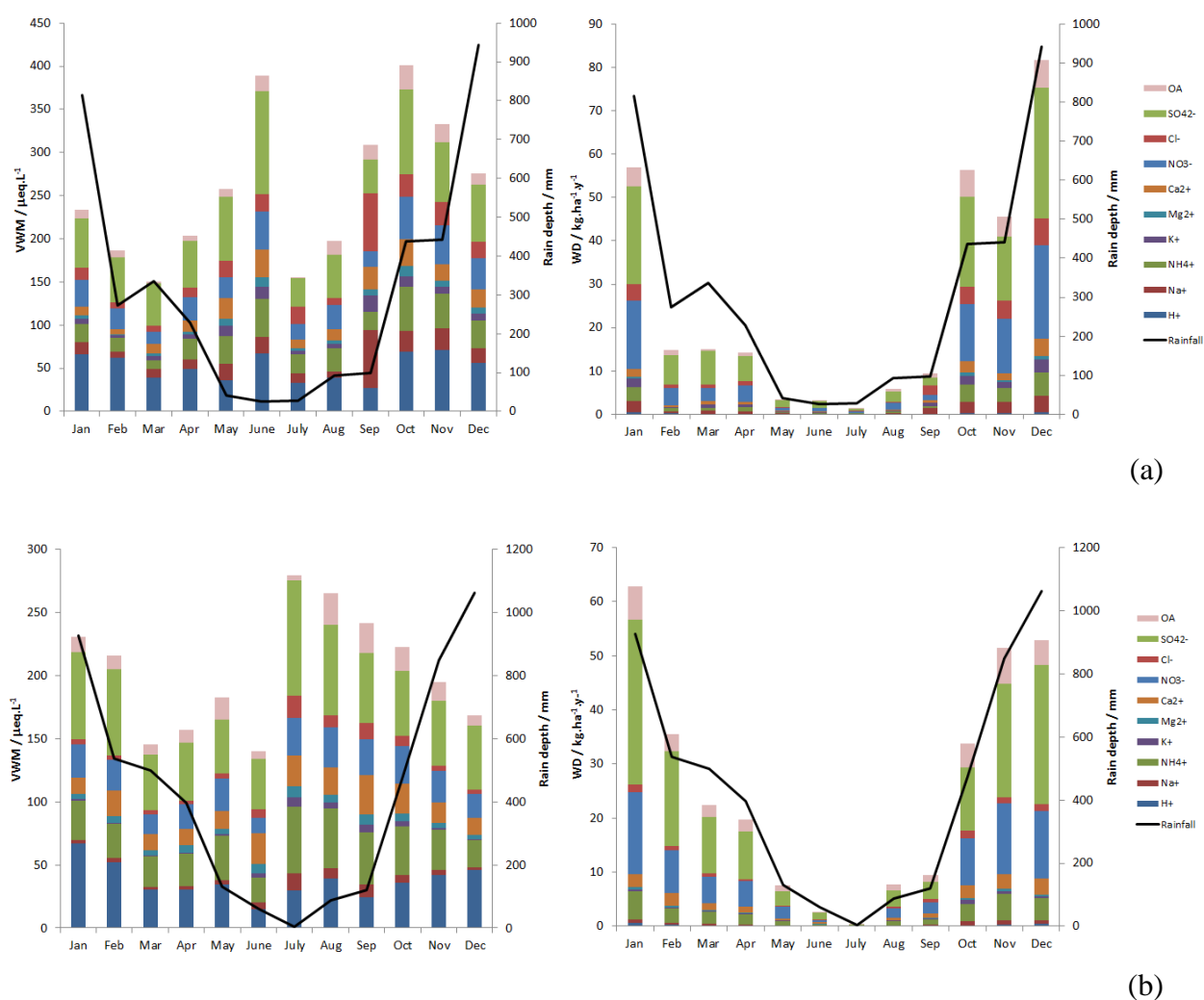
Figure 4.6: The rainfall depth and seasonal variability of individual ions to the VWM and WD values at (a) AF, (b) VT, (c) LT and (d) SK

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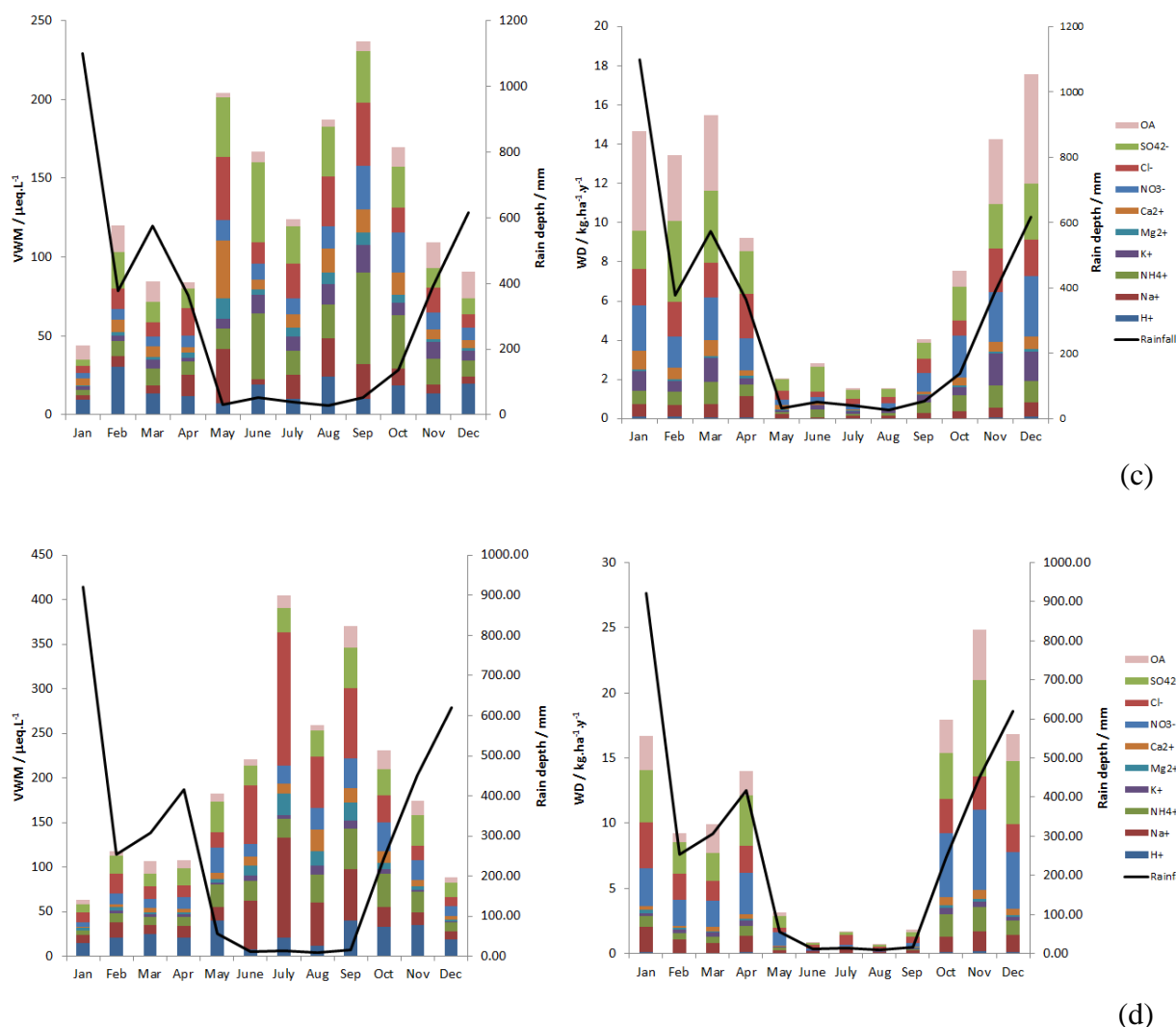
Figure 4.6 (continued): The rainfall depth and seasonal variability of individual ions to the VWM and WD values at (a) AF, (b) VT, (c) LT and (d) SK

As can be expected, it is clear from Fig. 4.6 that the ionic concentrations and fluxes of wet deposition closely correlate with the rainfall depth, i.e. significantly higher VWM ionic concentrations during the dry season and much higher wet deposition fluxes during the rainy season. This observation is in agreement with the occurrence that large rainfall events are normally associated with lower VWM ionic concentrations due to the cleansing of the atmosphere by rain drops. It is expected that atmospheric concentrations of these species will increase during the dry season due to the decrease in wet removal thereof, with dry deposition and chemical transformation being the main removal mechanisms. Strong variations in the chemical composition between different seasons are evident. This might be ascribed to the very large influence of anthropogenic activities, especially at the VT and AF sites. The dry winter season in South Africa is characterised by increased atmospheric pollutant concentrations due to the existence of more pronounced inversion layers trapping

pollutants near the surface of the earth. For SK (Fig. 4.6(d)), a strong marine signal (Na^+ and Cl^-) is obvious during the dry months of June, July, August and September, which can be linked to the meteorological conditions prevailing during these months. These increased Na^+ and Cl^- VWM concentrations associated with a cold front from the southern ocean passing over the country are also observed at LT and AF during the dry season, while even VT indicates slightly higher Na^+ and Cl^- VWM concentrations during the dry season. It was expected to also observe a strong seasonal signal for biomass burning (OA) from July to September at LT, but it was not observed. This can possibly be attributed to the influence of biomass burning for space heating and cooking, which is common in South Africa. A strong NH_4^+ signal is observed at this site for September and October, which can probably be linked to the beginning of the growth season (spring) and an increase in temperatures.

3.6 Comparison to previous measurements

In Fig. 4.7 and Table 4.7, the average annual ionic concentration, fluxes and pH values of wet deposition determined at AF, LT and SK in this investigation are compared to previous sampling periods at these sites (Mphepya *et al.* 2004 and 2006). Ionic concentrations and fluxes of wet deposition for the VT site are also included in order to assist in the contextualisation of the results.
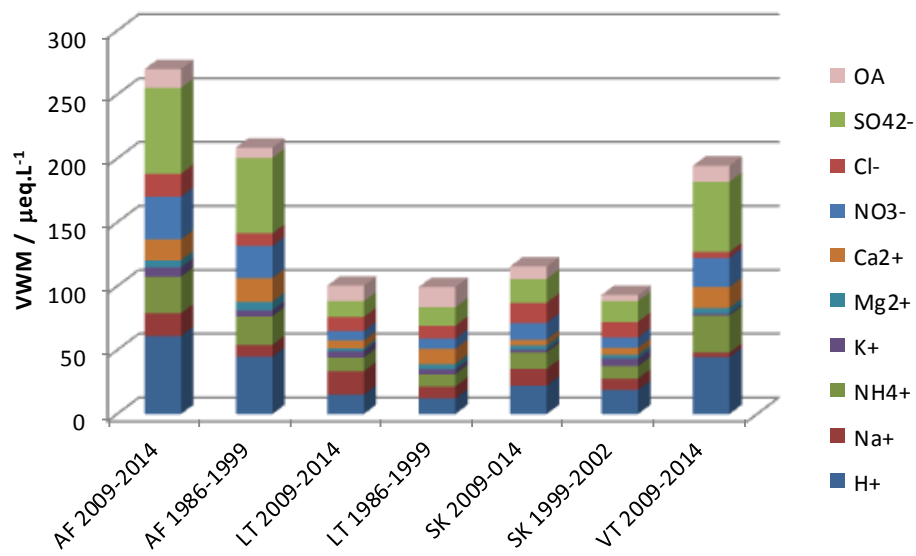
(a)
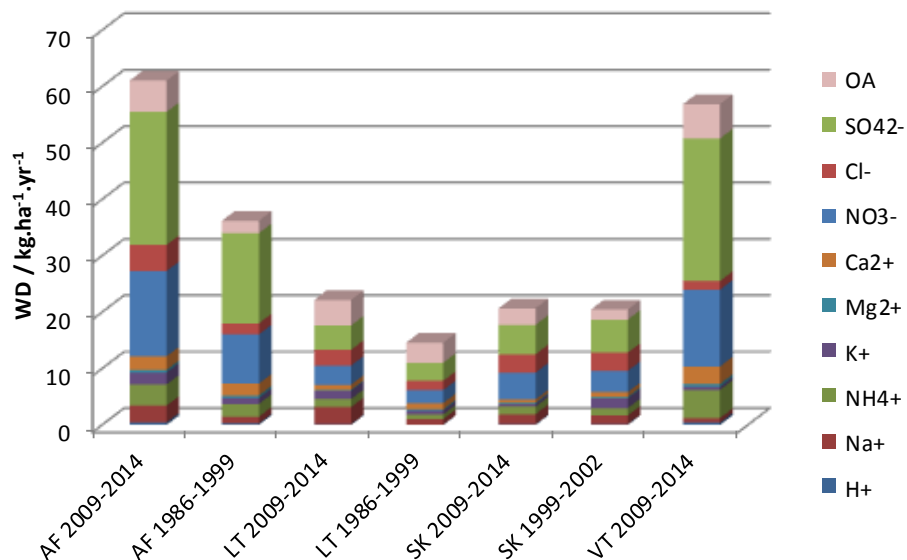
(b)

Figure 4.7: (a) VWM and (b) average annual WD determined between 2009 and 2014 at AF, VT, LT and SK, between 1986 and 1999 at AF and LT (Mphepya et al., 2004), and between 1999 and 2002 at SK (Mphepya et.al., 2006)

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Table 4.7: Comparison of pH, S and N values determined during the 2009 - 2014 time period at AF, VT, LT and SK, with that determined from 1986 – 1999 at AF and LT (Mphepya et al., 2004) and from 1999-2002 at SK (Mphepya et al, 2006)

	Amersfoort 2009-2014	Amersfoort 1986-1999	Louis Trichardt 2009-2014	Louis Trichardt 1986-1999	Skukuza 2009-2014	Skukuza 1999-2002	Vaal Triangle 2009-2014
	WD / kg.ha^{-1}.yr^{-1}	WD / kg.ha^{-1}.yr^{-1}	WD / kg.ha^{-1}.yr^{-1}	WD / kg.ha^{-1}.yr^{-1}	WD / kg.ha^{-1}.yr^{-1}	WD / kg.ha^{-1}.yr^{-1}	WD / kg.ha^{-1}.yr^{-1}
pH	4.32	4.35	4.89	4.91	4.66	4.75	4.51
N in NH_4^+	2.91	1.76	1.11	0.63	1.04	1.02	3.89
N in NO_3^-	3.41	1.97	0.76	0.52	1.08	0.85	3.08
S in SO_4^{2-}	7.87	5.33	1.44	1.07	1.75	1.96	8.44
Total no of events	323	437	157	223	257	146	445
Total collected rainfall (mm)	3800.4	7321.3	3828.7	6012.2	3323.1	2249.5	5146.1
Average annual rainfall (mm)	729.75	563.2	728.2	462.5	583.23	749.8	956.43

As shown in Fig. 4.7, it is evident that the total VWM ionic concentration and flux of wet deposition at AF were much higher during 2009-2014 than during 1985-1999. The total VWM ionic concentration increased by a factor of approximately 1.25, while the total wet deposition flux increased by a factor of approximately 1.71. Ionic concentrations are considered to be a better indication of change in the atmospheric chemical composition between these two periods, since wet deposition fluxes also depend on the rainfall amount. The increase in the VWM concentrations of SO_4^{2-}, NO_3^- and NH_4^+ observed at AF can be attributed to increased anthropogenic activities and population growth. Electricity consumption can be considered to be a good indicator of an increase in anthropogenic activities. As mentioned, the Mpumalanga Highveld holds nine coal-fired power stations, which generate approximately 90% of the electricity in South Africa (Fig. 2.7, Chapter 2) (Burton & Winkler, 2014). Electricity consumption in South Africa increased with 131 024 GWh from

1993 to 2006 (Inglesi & Blignaut, 2011). In addition, South Africa also experienced a period of economic growth from 2000, which also coincided with increases in production, especially in the pyrometallurgical industries (e.g. ICDA, 2012). Although, from a very low base compared to SO_4^{2-} and NO_3^-, an increase in the VWM concentrations of Na^+, Cl^- and K^+ is also observed, with the Na^+ and Cl^- ions almost two times higher during the period from 2009 to 2014. Since Na^+ is commonly assumed to be purely of marine origin and Cl^- is highly correlated with Na^+, this increase can only be attributed to an increase in marine air masses passing over AF (e.g. a slight change in rainfall patterns). However, this explanation must be substantiated through further investigation. Ca^{2+} and Mg^{2+} were slightly lower during 2009 to 2014. As Ca^{2+} and Mg^{2+} are considered to be mainly from crustal sources, this observation can be attributed to lower levels of atmospheric dust and higher average rainfall amounts during 2009-2014 than during 1986-1999.

The total VWM concentrations of the ten ions at LT during 1986-1999 and 2009-2014 were similar. The total wet deposition flux of the ten ions shows an increase for the 2009 to 2014 period when compared to the 1986 to 1999 period (Table 4.7), which can be ascribed to a significant increase in the average annual rainfall. Therefore, although SO_4^{2-} and NO_3^- show an increase in wet deposition fluxes between the two periods, the ionic concentrations of the species were actually slightly lower for the 2009 to 2014 period. The NH_4^+ concentration was marginally higher during 2009-2014. As mentioned previously, LT is a regional background site that is removed from the industrial activities in the interior of South Africa. The wet deposition chemistry results determined at LT for the two periods therefore indicate that the increase in total VWM ionic concentrations observed for wet deposition over the industrialised interior of South Africa over the 2009 to 2014 period did not have a similar impact on wet deposition chemistry at LT.

The total VWM ionic concentration of the measured ions at SK increased from 1999-2002 to 2009-2014, with the wet deposition flux being similar for the two periods due to lower rainfall amounts during the 2009-2014 period. The VWM concentrations of SO_4^{2-}, NO_3^- and NH_4^+ measured during the 2009 to 2014 period were also higher at SK, although to a lesser extent than at AF. The observation that SO_4^{2-} was the species with the highest VWM concentration for both periods at this site indicates that although SK is also considered to be a regional background site, it is affected by anthropogenic pollution from the industrialised Highveld. This is also indicated by the overlay back trajectories in Fig.3.2, Chapter 3.

Wet deposition flux of S at AF increased from 5.33 kg ha^{-1} yr^{-1} during 1986-1999 to 7.87 kg ha^{-1} yr^{-1} during 2009-2014, while the N flux increased from 3.66 kg ha^{-1} yr^{-1} to 6.01 kg ha^{-1} yr^{-1} (Table 4.7). In addition to higher VWM concentrations measured for SO_4^{2-}, NH_4^+, and NO_3^-, this increase can also

partially be ascribed to the increase of rainfall amount (by a factor of 1.3). At Louis Trichardt, wet deposition fluxes of S and N increased from 1.07 to 1.44 kg S ha^{-1} yr^{-1} and from 1.15 to 1.87 kg N ha^{-1} yr^{-1}, respectively. S deposition was slightly lower at SK, while N deposition was marginally higher.

Annual average pH did show significant differences among 1986-1999, 1999-2002 and 2009-2014 at all the sites (Table 4.7). However, the pH distribution of wet deposition samples (Fig. 4.2) indicates a higher percentage of the rain with lower pH during 2009-2014. During 1986 to 1999, the highest frequency of rain events was between 4.3 and 4.5 at AF, with only 8% of rain events having pH values lower than 4.0 (Mphepya *et al.*, 2004). At LT, the largest number of rain events had pH values ranging between 4.6 and 5.0 during 1986 to 1999. No rain samples had pH values lower than 4, while 6% of rainfall events had pH values higher than 6.0 (Mphepya *et al.*, 2004). A comparison of these two sampling periods at AF and LT indicates significant increases in rain events with lower pH values. A comparison of the 2009 to 2014 sampling period and the 1999 to 2002 sampling period at SK indicates a 2% increase in rain events with pH values lower than 4.0, with rain events higher than 6.0 remaining almost the same. The pH distribution of wet deposition samples indicated pH values ranging between 4.4 and 5.4 with the highest number of rain events having pH values of 5.2 for the 1999 to 2002 sampling period (Mphepya *et al.*, 2006). A large shift in the frequency distribution is observed at SK for the 2009 to 2014 sampling period with more rainfall events with lower pH values and the peak number of events observed between 4.4 and 4.6.

The potential contributions of mineral acids at AF and LT calculated by Mphepya *et al.* (2004) were 90 and 50%, respectively, while Mphepya *et al.* (2006) calculated that mineral acids contributed 81.5% at SK. Lower potential acidic contributions of mineral acids were calculated for the 2009 to 2014 period at AF and SK, which can possibly be ascribed to an increase in household combustion over the Mpumalanga Highveld that can be associated with an increase in organic acids. However, at LT, a decrease in the acidic contribution of organic acids is observed, which can possibly be attributed to an increased contribution from anthropogenic emissions.

4   Conclusions

The work presented here is the first comprehensive analysis of wet deposition in South Africa after the work presented by Mphepya *et al.* (2004; 2006). The value and necessity of long-term deposition monitoring programmes are clearly indicated in this chapter and by comparison to previous reported results. The calculation of the annual VWM ionic concentrations and fluxes of wet deposition for all of the sites in this study indicated that concentrations of the species largely from human emissions (including SO_4^{2-}, NH_4^+ and NO_3^-) were much higher during 2009-2014 than during 1986-1999 and

1999-2002. By comparing inter annual results reported in this chapter, it is evident that it is speculative to draw conclusions from the rainfall events for just one season. The large differences between sites also emphasise the importance of regionally representative spatial information.

The VWM ionic concentrations of species emitted by anthropogenic activities were much higher at VT and AF, than at SK and LT. The concentrations of maritime species were higher at SK and LT. The results of back-trajectory analyses confirm that air pollutants released from anthropogenic sources would transport to rural regions.

Several empirical and statistical methods were used to determine the major sources of the ten ions in wet deposition. The major five sources are marine, terrigenous, fossil fuel combustion, agriculture and biomass burning. Empirical methods indicated that marine was the largest contributor to Na^+, Cl^- and Mg^{2+} at SK and LT, lower at AF and very low at VT. PCA and clustering of the chemical composition data confirmed these observations and provided a theoretical tool to identify different source groups. Terrigenous (crustal) contributions were confirmed with the empirical methods and PCA. The five-year dataset allowed for the identification of different inter-annual and seasonal trends that further enhance the knowledge on atmospheric chemical processes in southern Africa. From the results presented, it is clear that anthropogenic (fossil fuel combustion and agriculture) sources dominate the chemical composition of wet deposition at VT and AF, while also significantly influencing wet deposition chemistry at relatively remote sites (SK and LT). Although the empirical and statistical methods applied in this study could adequately identify source group contributions, it is recommended that in future studies more advanced methods such as positive matrix factorisation should be utilised in wet deposition studies from which the contribution of each source to each ion could be more accurately established (Qiao *et al.*, 2015).

An overall increase of wet deposition fluxes of species associated with anthropogenic activities in South Africa, i.e. SO_4^{2-}, NO_3^- and NH_4^+, was observed at the sites when the 2009 to 2014 results were compared to previous data reported by Mphepya *et al.* (2004; 2006). This increase can most likely be ascribed to the increase in anthropogenic activities in South Africa. Concurrently, the annual H^+ concentration increased since the previous reports, which is reflected in a shift to more acidic rain events at all the South African IDAF sites. Acidic potential calculations indicated that only 22 to 42% of the measured H^+ concentrations were neutralised by alkaline species at the various sites.

Chapter 5: Total dry gaseous and wet deposition of nitrogen and sulphur compounds

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In this chapter, the deposition results obtained from gaseous measurements (Chapter 3) and from precipitation measurements (Chapter 4) are combined to estimate the total dry gaseous and wet nitrogen and sulphur deposition. Since the precipitation measurements for this study only started in 2009, this chapter will only focus on the total annual average deposition results for the period 2009-2014.

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1   Total deposition of dry gaseous and wet nitrogen compounds

Dry deposition fluxes at the SA DEBITS sites were calculated using estimated dry deposition velocities from Adon, *et al.,* 2013, combined with measured concentrations of gaseous nitrogen species using passive samplers for NO_2, NH_3 and HNO_3. Wet deposition fluxes were calculated by multiplying the annual volume weighted mean (VWM) with the total annual rainfall depth at each site and the molar mass (equivalent weight) of the specific ion (e.g. NH_4^+ and NO_3^-).

Figure 5.1 illustrates the total annual average gaseous and wet N deposition for the period 2009-2014 at the four SA DEBITS sites and Figure 5.2 indicates the percentage contribution per individual compound. From Figure 5.1, it is clear that dry deposition appears to be the dominant contributor to total deposition. According to the calculations described in Chapters 3 and 4, dry gaseous deposition accounted for 73% of the gaseous and wet N deposition at VT, 62% at AF, 67% at SK and 68% at LT. These values are in good agreement with the values reported in a recent global assessment based on concentration measurements and modelling results, where dry deposition in Africa accounts for 60 – 70% of the total nitrogen deposition in South Africa (Vet *et al.,* 2014). The results from previous South African studies (Mphepya *et al.*, 2002 and Martins, 2009) that was included in the assessment, indicated that dry deposition contributed about 50% of the total at AF and about 60% at LT and SK. The use of one single deposition velocity (V_d) for nitrogen is a very crude assumption and is identified as a serious

shortcoming (see Chapter 6) estimating dry deposition of especially nitrogen deposition at this stage and will be the topic of future studies.

According to this study, the total dry gaseous and wet N deposition in kgN/ha/yr was 16.7 at VT, 10.2 at AF, 4.2 at SK and 4.0 and LT. By using modelled dry deposition of N-oxidized and N-reduced with measurement-based inferential estimates from 2000 to 2007, values of 9.7, 5.6 and 4.2 kgN/ha/yr for AF, SK and LT is reported by Vet *et al.*, 2014 which is in excellent agreement with the results reported in this study.

Annual average total N deposition for 2009 - 2014

	VT	AF	SK	LT
■ Total Wet	7,0	6,3	2,1	1,9
■ Total Dry	16,7	10,2	4,2	4,0

Figure 5.1: The annual average total dry gaseous and wet N deposition for the period 2009 – 2014 at Vaal Triangle (VT), Amersfoort (AF), Skukuza (SK) and Louis Trichardt (LT).

The contribution from the different dry gaseous and wet N species are given in Figure 5.2. The differences in % species contribution between sites are rather significant as for instance the much higher %NO_2 (32) at the Vaal Triangle site than at the other three sites. This may be ascribed to large volumes of traffic and NO_2 emitting industrial sources in the vicinity of this site. It follows from the pie-charts in Figure 5,2 that on average, NO_3^- contribute about 25%, NH_4^+ 26%, HNO_3 20%, NO_2 15% and NH_3 14% to the total N deposition budget.

Chapter 5
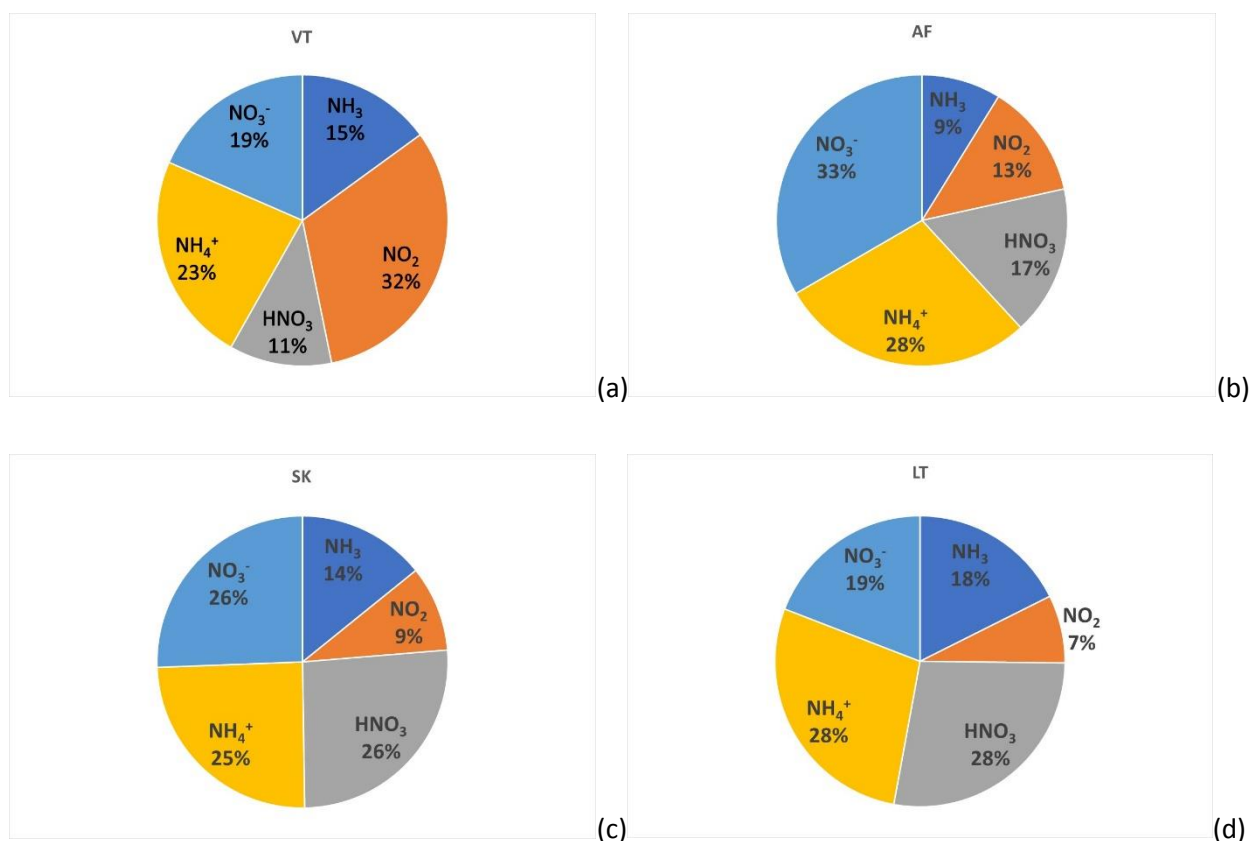
Figure 5.2: The % species composition to the annual average total dry gaseous and wet nitrogen deposition for the period 2009-2014 at (a) Vaal Triangle, (b) Amersfoort, (c) Skukuza and (d) Louis Trichardt

2 Total deposition of dry gaseous and wet sulphur compounds

Similar as for the nitrogen compounds, dry sulphur deposition fluxes at the SA DEBITS sites were estimated using deposition velocities from Adon *et al.,* 2013, combined with measured concentrations of gaseous SO_2 using passive samplers. Wet deposition fluxes were estimated by multiplying the annual volume weighted mean (VWM) with the total annual rainfall depth at each site and the molar mass (equivalent weight) of the specific ion (SO_4^{2-}).

Figure 5.3 illustrates the annual average total dry gaseous and wet S deposition for the period 2009 – 2014 at the four SA DEBITS sites. In comparison to modelled predictions of total sulphur deposition in Vet *et al.,* (2014), the values for dry deposition at the VT and AF sites are high (7.1 and 4.6 kgS/ha/a respectivily) and of the same order of magnitude as estimations for east Asia, western Europe and North America. The values for SK and LT and is in accordance with the predictions for South Africa of between 0.9 – 1.4 kgS/ha/a in the global assessment (Vet *et al.,* 2014).

The total dry gaseous and wet sulphur deposition calculated for VT, AF, SK and LT in this study was 15.5, 12.4, 2.8, and 2.3 kgS/ha/a, respectively. The percentage contribution of S by dry gaseous deposition also dominated the wet deposition, with 46%, 37%, 36% and 39% at VT, AF, SK and LT, respectively. This again is slightly lower than the estimates in the global assessment, with report values between 45 and 60% by dry deposition in Africa (Vet, *et al.,* 2014). This slightly lower value of gaseous dry deposition can be attributed to the deposition velocity used in this study.

Annual average total S deposition for 2009 - 2014

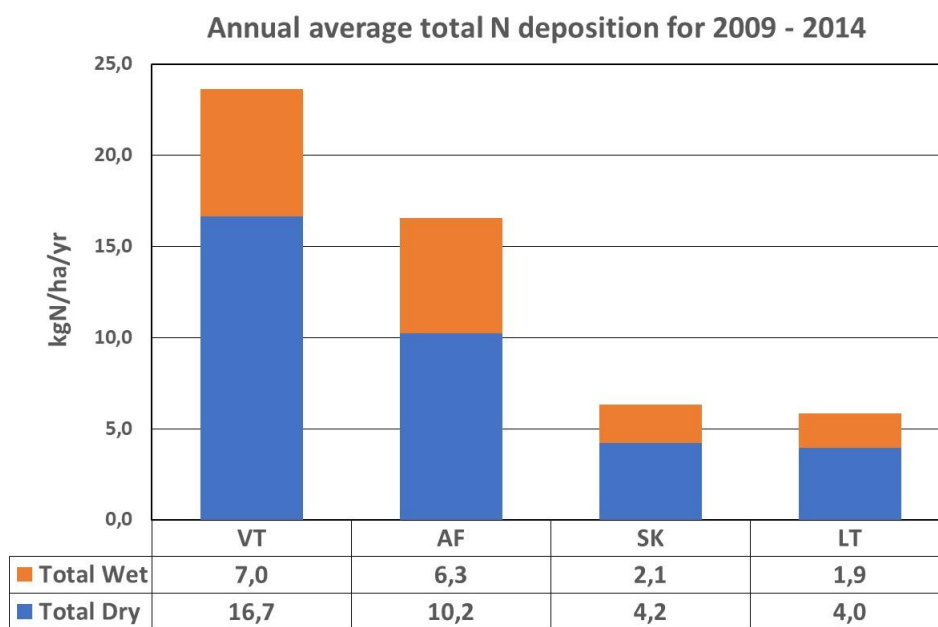|	VT	AF	SK	LT
SO42-	8,4	7,9	1,8	1,4
SO2	7,1	4,6	1	0,9
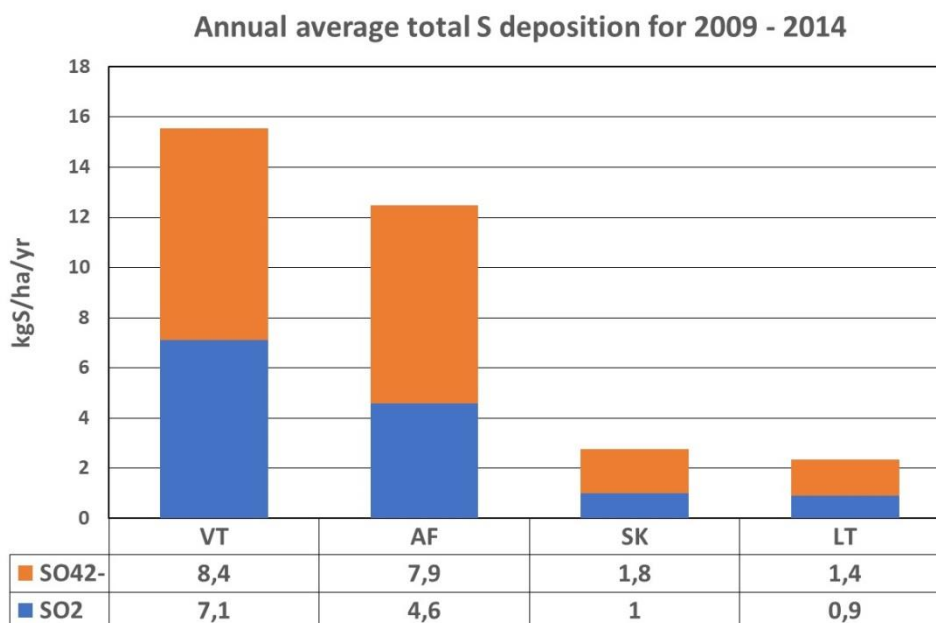
Figure 5.3: The annual average total dry gaseous and wet S deposition for the period 2009-2014 at Vaal Triangle (VT), Amersfoort (AF), Skukuza (SK) and Louis Trichardt (LT).

Chapter 6: Critical assessment and concluding remarks

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In this chapter, the contribution of the current study will be critically evaluate, as well as to what extent the motivation and statement of need for the current study have been addressed. Furthermore, this chapter will also focus on the most important recommendations from each of the chapters and remaining gaps will be identified and recommendations made to aid future research in South Africa on related topics.

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1 Assessment of the study objectives

This section will focus on the evaluation of the contribution to the study in terms of the objectives as they were listed in Chapter 1. Furthermore, the study objectives will be evaluated as per the contribution they make in this field of study and the study limitations will be described. The general aim of this study was to measure the concentrations of selected gaseous species (using passive samplers) and to quantify the concentrations of chemical species in rainwater. This aim was set to address the need for available research data for South Africa, as part of the African continent (refer to section 4.1, Chapter 1).

1.1 Research objective 1

Determine the long-term ambient concentrations of selected inorganic gaseous species, namely SO_2, NO_2, O_3, HNO_3 and NH_3, at four sites in the South African interior

This objective was addressed in Chapter 3 of this study. The measurement of the selected gaseous species was conducted at Louis Trichardt (LT) (1995-2014), Amersfoort (AF) (1997-2014), Skukuza (SK) (2000-2014) and the Vaal Triangle (VT) (2008-2014) for SO_2, NO_2, O_3, and NH_3. Measurements for HNO_3 started in 2003 at LT, AF and SK, and in 2008 at VT. Due to the distance between the sites, the help of non-specialist operators at each site was needed to mount the samplers and to replace them on a monthly basis. Correct handling of the samplers, as well as sealing and storage of the samplers to prevent contamination therefore remain big concerns and variables that cannot be controlled. Another

observation that was made during the study was that it sometimes happens that the duplicate samplers deliver different concentrations. This created a dilemma that was difficult to solve since only two samplers were used.

1.2   Research objective 2

Determine the chemical composition and concentrations of precipitation (specifically the following ionic species: acetic acid, propionic acid, formic acid, chloride, sulphate, nitrate, oxalic acid, sodium, potassium, magnesium, calcium and ammonium) at all sites considered

Results obtained from precipitation measurements were presented in Chapter 4. The chemical composition and concentrations of precipitation were determined at all sites from 2009 to 2014. In this time period, a total number of 1 182 samples were collected. Data loss due to analytical errors accounted for 3.2%, while a further 12.7% of the samples did not pass the WMO ID% criteria. The data coverage therefore amounted to 84.1%.

The VWM values of the organic acids were combined in the results in this study since it was difficult to obtain an acceptable resolution between acetic acid, propionic acid and formic acid during analysis in this study. Due to the sensitivity of organic acids to biodegradation, difference in site operations influences these results and large fluctuations were sometimes observed in die organic acid concentrations at sites. This caused a more cautious interpretation of the results presented for these species.

1.3   Research objective 3

Estimate the dry gaseous and wet deposition of the measured sulphur and nitrogen species at the selected sites

Dry gaseous deposition was estimated and presented as part of Chapter 3, while wet deposition was calculated and presented in Chapter 4. The wet deposition was calculated by multiplying the annual volume weighted mean (VWM) with the total annual rainfall depth at each site and the molar mass (equivalent weight) of the specific ion. The dry gaseous deposition was calculated using estimated deposition velocities (V_d) from literature for each of the selected gaseous species. The dry gaseous deposition calculations were subjected to a few limitations linked to the absence of accurate site specific

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V_d values. In the case of N species, only the downward flux was considered and not bi-directional exchange, differences in V_d values for the different seasons were not taken into account. These limitations may have significant implications on the reported values and it will be important to directly measure deposition velocities at the different sites at different seasons to improve the accuracy of the reported values. Due to equipment and other financial limitations, this was not possible to perform these measurements in this study.

1.4   Research objective 4

Evaluate differences in concentrations (for both trace gases as well as precipitation) between the selected sites

The differences in ionic concentrations measured in gaseous species as well as precipitation were evaluated in this study. Contributing factors to these differences were identified and discussed in Chapters 3 and 4 (e.g. air transport of pollutant species from the industrialised Highveld region over sites, direction from where air masses originated, influence from nearby point sources, tourism, local legislation and economy). Although the differences could be ascribed to a number of influencing factors, the differences in concentrations observed between the various sites are most likely the cumulative effect from various factors (some of which might not have been covered/evaluated in the study). Methods by which the source group estimations can be improved, should be addressed in future studies.

1.5   Research objective 5

Evaluate temporal differences in concentrations at the selected sites

The value of the long-term ambient concentrations was evaluated in Chapter 3 for each of the selected inorganic gaseous species. It was, however, more difficult to compare the seasonal differences at the VT site to the other sites. The influence from the highly industrialised region overshadows any seasonal changes in the VT and makes it difficult to evaluate differences in concentrations. Large inter-annual variations in the ionic concentrations and fluxes of wet deposition were observed between the sites, emphasising the importance of a good spatial coverage when establishing regions that are environmentally at risk (Chapter 4).

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1.6   Research objective 6

Calculate source group contributions of the above-mentioned species at the selected sites

Source group estimations were determined in Chapter 4 by using only precipitation data. Similar or supporting calculations using the data available from the gaseous measurements could not be performed due to the unavailability of good emission data bases and limited number of gaseous species monitored. Trends in the long-term data in Chapter 3 could therefore only be linked to limited factors or point sources that might possibly influence the observations and no clear source group estimations could be performed. It is possible to evaluate source group estimations via principle component analysis, for instance, but this route was not followed for the current study. In future studies, the measurement of certain isotopes or tracers for each of the different sources (e.g. Levoglucosan as a tracer for biomass burning) could be considered to enable a better estimation of the contribution of these sources.

2   Evaluation of the motivation/statement of need

The main concerns that have been raised in the motivation/statement of need in Chapter 1 include the following:

- The need for long-term atmospheric monitoring systems to address the concern about potential adverse environmental effects due to anthropogenic emissions;
- The limited amount of research that has been conducted in South Africa in this field (a gap has been identified in a recent global assessment (Vet *et al.*, 2014));

These concerns were addressed in this study. Long-term data is now available for the selected gaseous species and has been evaluated in Chapter 3 of this thesis. The study contributed greatly with new data on precipitation chemistry in South Africa at various sites and this data has also been published recently.

3 Recommendations and future perspectives

New data was generated by this study and the interpretation thereof contribute to the understanding of dry and wet deposition characteristics in the region. In this regard, gaps that were identified in previous studies (Mpheya *et al.*, 2004, Martins *et al.*, 2007, Adon *et al.*, 2010) and global assessments (Vet *et al.*, 2014) was addressed. However, a few areas were identified that need improvement and future studies conducted in this field must aim to address and incorporate these recommendations.

The first recommendation is regarding deposition velocities. Future studies will improve on the quality of data generated if deposition velocities are measured at each site, instead of using values from literature. It is well-known that deposition velocities are coupled with large uncertainties. Therefore, measured values (and also different values for dry and wet seasons) would limit uncertainties. Furthermore, it would be advised that future studies should also focus on bidirectional exchange and not just the downward deposition.

The second recommendation is regarding the data interpretation. Comparisons between sites could be more effective if measured data is compared to emission inventories. It would also be recommended to conduct isotope research on pollutant plume transport in order to estimate the impact of pollution from priority areas to surrounding areas. Another means of conducting an impact assessment would be to run forward trajectories to determine the transport pathways from the measurement sites, similar to what was done by Piketh and Prangley in 1998 (Figure 2.2, Chapter 2).

Thirdly, new or other methods to improve source group estimations needs to be investigated. Principal component analysis proved to be effective in Chapter 4 of this study, but the use of positive matrix factorisation is strongly recommended, since this method establishes the contribution of each source to each ion.

The last recommendation is to also incorporate aerosol and organic nitrogen measurements in future studies in order to determine the total deposition. Aerosol measurements was beyond the scope of the current study and the determination of atmospheric organic nitrogen at the remote sites is beyond the capacity of the research group at this stage.

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Appendix A

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SO₂ contextualisation

South Africa		African continent		Global	
Value	Site name & Reference article	Value	Site name & Reference article	Value	Site name & Reference article
7.0	Vanderbijlpark – *Lourens *et al.*, 2011	0.0	Mt Kenya – *Carmichael *et al.*, 2003	13.1	Linan – *Carmichael *et al.*, 2003
5.0	Balfour – *Lourens *et al.*, 2011	0.1	Tamanrasset – *Carmichael *et al.*, 2003	0.8	Shui-Li – *Carmichael *et al.*, 2003
5.2	Standerton – *Lourens *et al.*, 2011	0.1	Banizoumbou – *Carmichael *et al.*, 2003	0.3	Oki – *Carmichael *et al.*, 2003
5.5	Amersfoort – *Lourens *et al.*, 2011	0.1	Lamto – *Carmichael *et al.*, 2003	0.1	Tanah Rata – *Carmichael *et al.*, 2003
5.5	Ermelo – *Lourens *et al.*, 2011	<0.03	Zoetele – *Carmichael *et al.*, 2003	0.2	Lawa Mandau – *Carmichael *et al.*, 2003
4.1	Carolina – *Lourens *et al.*, 2011	0.6	Camkoru – *Carmichael *et al.*, 2003	0.0	Luang Prabang – *Carmichael *et al.*, 2003
13.3	Witbank – *Lourens *et al.*, 2011	0.6	Banizoumbou – *Adon *et al.*, 2010	0.2	Nagarkot – *Carmichael *et al.*, 2003
8.7	Delmas – *Lourens *et al.*, 2011	0.6	Katibougou – *Adon *et al.*, 2010	4.8	Cochin – *Carmichael *et al.*, 2003
7.0	Elandsfontein – *Carmichael *et al.*, 2003	1.0	Agoufou – *Adon *et al.*, 2010	1.8	Agra – *Carmichael *et al.*, 2003
0.3	Cape Point – *Carmichael *et al.*, 2003	0.5	Lamto – *Adon *et al.*, 2010	0.1	Petit Saut – *Carmichael *et al.*, 2003
2.8	Amersfoort – *Adon *et al.*, 2010	0.8	Djougou – *Adon *et al.*, 2010	<0.03	Ushuaia – *Carmichael *et al.*, 2003
0.8	Louis Trichardt – *Adon *et al.*, 2010	0.3	Zoetele – *Adon *et al.*, 2010	0.2	El-Tololo – *Carmichael *et al.*, 2003
0.7	Cape Point – *Adon *et al.*, 2010	0.4	Bomassa – *Adon *et al.*, 2010	0.1	Arembepe – *Carmichael *et al.*, 2003
				3.1	Marcapomacocha – *Carmichael *et al.*, 2003
				68.2	Houma – *Meng *et al.*, 2010
				13.9	Lin'an – *Meng *et al.*, 2010
				72.3	Kaili – *Meng *et al.*, 2010
				40.3	Chenzhou – *Meng *et al.*, 2010
				4.2	Meixian – *Meng *et al.*, 2010

NO₂ contextualisation

South Africa		African continent		Global	
Value	Site name & Reference article	Value	Site name & Reference article	Value	Site name & Reference article
7.6	Vanderbijlpark – *Lourens *et al.*, 2011	2.4	Banizoumbou – *Adon *et al.*, 2010	26.6	Houma – *Meng *et al.,* 2010
3.0	Balfour – *Lourens *et al.*, 2011	1.9	Katibougou – *Adon *et al.*, 2010	12.6	Lin'an – *Meng *et al.*, 2010
6.2	Standerton – *Lourens *et al.*, 2011	1.8	Agoufou – *Adon *et al.*, 2010	8.5	Kaili – *Meng *et al.*, 2010
2.9	Amersfoort – *Lourens *et al.*, 2011	1.0	Lamto – *Adon *et al.*, 2010	19.5	Chenzhou – *Meng *et al.*, 2010
6.6	Ermelo – *Lourens *et al.*, 2011	1.2	Djougou – *Adon *et al.*, 2010	10.3	Meixian – *Meng *et al.*, 2010
2.1	Carolina – *Lourens *et al.*, 2011	0.9	Zoetele – *Adon *et al.*, 2010	1.7	Ash Mountain, California – *Bytnerowicz *et al.*, 2002
8.6	Witbank – *Lourens *et al.*, 2011	1.4	Bomassa – *Adon *et al.*, 2010	1.3	Crystal Cave, California – *Bytnerowicz *et al.*, 2002
9.2	Delmas – *Lourens *et al.*, 2011			2.0	Lower Kaweah, California – *Bytnerowicz *et al.*, 2002
2.5	Amersfoort – *Adon *et al.*, 2010				
0.7	Louis Trichardt – *Adon *et al.*, 2010				
1.2	Cape Point – *Adon *et al.*, 2010				

Appendix A

NH₃ contextualisation

South Africa		African continent		Global	
Value	Site name & Reference article	Value	Site name & Reference article	Value	Site name & Reference article
2.0	Elandsfontein – *Carmichael *et al.*, 2003	1.0	Mt Kenya – *Carmichael *et al.*, 2003	5.0	Linan – *Carmichael *et al.*, 2003
1.0	Cape Point – *Carmichael *et al.*, 2003	4.0	Tamanrasset – *Carmichael *et al.*, 2003	7.0	Shui-Li – *Carmichael *et al.*, 2003
1.2	Amersfoort – *Adon *et al.*, 2010	4.0	Banizoumbou – *Carmichael *et al.*, 2003	<1	Oki – *Carmichael *et al.*, 2003
1.2	Louis Trichardt – *Adon *et al.*, 2010	3.0	Lamto – *Carmichael *et al.*, 2003	<1	Tanah Rata – *Carmichael *et al.*, 2003
1.5	Cape Point – *Adon *et al.*, 2010	2.0	Zoetele – *Carmichael *et al.*, 2003	<1	Lawa Mandau – *Carmichael *et al.*, 2003
		<1	Camkoru – *Carmichael *et al.*, 2003	3.0	Luang Prabang – *Carmichael *et al.*, 2003
		6.3	Banizoumbou – *Adon *et al.*, 2010	2.0	Nagarkot – *Carmichael *et al.*, 2003
		6.6	Katibougou – *Adon *et al.*, 2010	19.0	Cochin – *Carmichael *et al.*, 2003
		7.4	Agoufou – *Adon *et al.*, 2010	>40	Agra – *Carmichael *et al.*, 2003
		4.0	Lamto – *Adon *et al.*, 2010	<1	Petit Saut – *Carmichael *et al.*, 2003
		3.9	Djougou – *Adon *et al.*, 2010	<1	Ushuaia – *Carmichael *et al.*, 2003
		4.2	Zoetele – *Adon *et al.*, 2010	<1	El-Tololo – *Carmichael *et al.*, 2003
		4.7	Bomassa – *Adon *et al.*, 2010	<1	Arembepe – *Carmichael *et al.*, 2003
				3.0	Marcapomacocha – *Carmichael *et al.*, 2003
				13.9	Houma – *Meng *et al.,* 2010
				2.3	Lin'an – *Meng *et al.*, 2010
				6.4	Kaili – *Meng *et al.*, 2010
				4.1	Chenzhou – *Meng *et al.*, 2010
				6.2	Meixian – *Meng *et al.*, 2010

HNO₃ contextualisation

South Africa		African continent		Global	
Value	Site name & Reference article	Value	Site name & Reference article	Value	Site name & Reference article
0.9	Amersfoort – *Adon et al.*, 2010	0.5	Banizoumbou – *Adon et al.*, 2010		
0.2	Louis Trichardt – *Adon et al.*, 2010	0.4	Katibougou – *Adon et al.*, 2010		
0.5	Cape Point – *Adon et al.*, 2010	0.5	Agoufou – *Adon et al.*, 2010		
		0.3	Lamto – *Adon et al.*, 2010		
		0.4	Djougou – *Adon et al.*, 2010		
		0.2	Zoetele – *Adon et al.*, 2010		
		0.3	Bomassa – *Adon et al.*, 2010		

Appendix A

O₃ contextualisation

South Africa		African continent		Global	
Value	Site name & Reference article	Value	Site name & Reference article	Value	Site name & Reference article
15.7	Vanderbijlpark – *Lourens *et al.*, 2011	30.0	Mt Kenya – *Carmichael *et al.*, 2003	38.3	Linan – *Carmichael *et al.*, 2003
27.0	Balfour – *Lourens *et al.*, 2011	33.2	Tamanrasset – *Carmichael *et al.*, 2003	25.0	Shui-Li – *Carmichael *et al.*, 2003
18.3	Standerton – *Lourens *et al.*, 2011	25.7	Banizoumbou – *Carmichael *et al.*, 2003	40.4	Oki – *Carmichael *et al.*, 2003
23.3	Amersfoort – *Lourens *et al.*, 2011	14.9	Lamto – *Carmichael *et al.*, 2003	16.0	Tanah Rata – *Carmichael *et al.*, 2003
21.1	Ermelo – *Lourens *et al.*, 2011	7.2	Zoetele – *Carmichael *et al.*, 2003	17.0	Lawa Mandau – *Carmichael *et al.*, 2003
27.0	Carolina – *Lourens *et al.*, 2011	35.4	Camkoru – *Carmichael *et al.*, 2003	11.2	Luang Prabang – *Carmichael *et al.*, 2003
17.3	Witbank – *Lourens *et al.*, 2011	11.9	Banizoumbou – *Adon *et al.*, 2010	33.1	Nagarkot – *Carmichael *et al.*, 2003
16.3	Delmas – *Lourens *et al.*, 2011	12.6	Katibougou – *Adon *et al.*, 2010	11.8	Cochin – *Carmichael *et al.*, 2003
20.4	Amersfoort – *Josipovic, 2009	12.2	Agoufou – *Adon *et al.*, 2010	30.8	Agra – *Carmichael *et al.*, 2003
18.0	Harrismith – *Josipovic, 2009	10.9	Lamto – *Adon *et al.*, 2010	8.4	Petit Saut – *Carmichael *et al.*, 2003
15.5	Skukuza – *Josipovic, 2009	14.0	Djougou – *Adon *et al.*, 2010	16.7	Ushuaia – *Carmichael *et al.*, 2003
21.3	Kranskop – *Josipovic	4.8	Zoetele – *Adon *et al.*, 2010	30.6	El-Tololo – *Carmichael *et al.*, 2003
20.3	Heilbron – *Josipovic	4.0	Bomassa – *Adon *et al.*, 2010	19.2	Arembepe – *Carmichael *et al.*, 2003
14.5	Kroonstad – *Josipovic			25.1	Marcapomacocha – *Carmichael *et al.*, 2003
24.2	Louis Trichardt – *Josipovic			64.0	Ash Mountain, California – *Bytnerowicz *et al.*, 2002
35.1	Elandsfontein – *Carmichael *et al.*, 2003			52.0	Crystal Cave, California – *Bytnerowicz *et al.*, 2002
24.2	Cape Point – *Carmichael *et al.*, 2003			60.0	Lower Kaweah, California – *Bytnerowicz *et al.*, 2002
27.0	Amersfoort – *Adon *et al.*, 2010				
35.0	Louis Trichardt – *Adon *et al.*, 2010				
27.0	Cape Point – *Adon *et al.*, 2010				

Appendix A